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SULPHATE-REDUCTION WATER TREATMENT AT MOUNT PLEASANT:

PHASES I AND II

Dr. Tom A. Al
and
Nicolette Stanley

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Dr. Tom A. Al
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Nicolette Stanley

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Sulphate-reduction Water Treatment at Mount Pleasant:

Phase I

A Research Project to Assess the Potential for Bacterially Mediated Sulphate Reduction as a Method for Mine Water Treatment

By: Dr. Tom A. Al, and
Nicolette Stanley

Dept. of Geology, University of New Brunswick
P.O. Box 4400, Fredericton, NB E3B 5A3

March 1, 2002

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1. Introduction

1.1 Background

The research project is at the Mount Pleasant Mine site in southern New Brunswick. Mount Pleasant is a tin and tungsten mine that began production in 1983 and closed in 1985. The deposit contains a variety of metals including tungsten (W), tin (Sn), zinc (Zn), copper (Cu), and indium (In). Since closing, the mine portal has filled with ground water that contains elevated concentrations of lead (Pb), arsenic (As), and Zn. At present, the mine water flows from the portal at a rate of approximately 140 gal/min (0.63 m^3/min) and is treated with lime in an effort to lower the Zn concentration. The operation of the lime treatment process requires electrical power, and the maintenance of electrical service at the site is very expensive. Consequently, the New Brunswick Department of Natural Resources and Energy decided to conduct a research program to investigate the potential for establishing a passive treatment system that would not require electrical service. This research was implemented in November 2001 in collaboration with T. Al from the Department of Geology at the University of New Brunswick.

1.2 Objectives

The principal objective of the research program was to determine the feasibility of bacterially-mediated sulphate (SO_4) reduction as a passive treatment method to lower the metal concentrations in the drainage from the portal to acceptable levels. The feasibility of treatment would be based on the results of column experiments that are established at the mine site for pilot-scale treatment of the mine water. The following specific objectives are defined in order to meet the overall objective:

- assemble columns at the mine site and fill them with a mixture of coarse gravel and a reactive organic solid such as compost,
- establish a continuous flow of mine water through the columns, increasing the flow rate with time throughout the experiment,
- monitor the pH and redox conditions, as well as the SO_4 and metal concentrations at various points along the length of the columns

1.3 Treatment of Mine Drainage by Sulphate Reduction

Sulphide-mineral oxidation, and the resulting generation of metal-contaminated drainage water, is a common problem encountered when bedrock materials are excavated during mining activities. The problem usually occurs when the rock materials contain iron-sulphide minerals such as pyrite [FeS_2] and pyrrhotite [FeS], which are unstable in the presence of atmospheric oxygen and they react with oxygen, e.g.:

$$FeS_{2(s)} + {}^{15}/_{4}O_{2(gas)} + {}^{7}/_{2}H_2O \rightarrow Fe(OH)_{3(solid)} + 2SO_4{}^{2-}{}_{(aqueous)} + 4H^{+}{}_{(aqueous)} \qquad [1]$$

The excavation of these minerals, and the consequent increase in exposed sulphide-mineral surface area, results in a large increase in reaction rates compared to the natural condition where oxygen access to the minerals is limited. Heavy-metal contamination (e.g. copper, lead, zinc, cobalt, arsenic) results when sulphide minerals that contain these metals are also present in the rock materials and react with oxygen:

$$MeS_{(s)} + O_{2(gas)} \rightarrow Me^{2+}{}_{(aqueous)} + SO_4{}^{2-}{}_{(aqueous)} \quad [2]$$

where: Me represents metals such as copper (Cu), lead (Pb) and zinc (Zn)

The treatment of mine drainage by sulphate-reducing bacteria (SRB) is a biogeochemical process that reverses the effects of sulphide oxidation, and has been studied in field and laboratory settings (Blowes et al., 1995; Waybrant, 1995; Waybrant et al., 1995). The treatment is due to the ability of the bacteria to reduce sulphate to sulphide, which binds with most heavy metals to form insoluble precipitates:

$$Me^{2+} + SO_4{}^{2-} + 2CH_2O \rightarrow MeS_{(s)} + 2H_2CO_3{}^{\circ} \quad [3]$$

where: CH_2O represents organic carbon

When the metals are in this stable form they no longer contribute to the contamination of surrounding water systems (Lyew and Sheppard 2001). The SRB's are anaerobic bacteria that use simple organic compounds as electron donors for the reduction of sulphate (Gould 1994). This reaction has been attributed mostly to bacteria called *Desulfibrio sp.* (Tsukamoto and Miller 1999). If sulphate reduction can be achieved at Mount Pleasant, then it will lead to the removal of dissolved metals and sulphate from the drainage water. Although not apparent in reaction 3, sulphate reduction is generally accompanied by an increase in alkalinity as well (Waybrant et al., 1997).

2. Experimental Methods

2.1 Reactive Column Mixture

In order to achieve effective treatment, the columns must contain a permeable material that will promote the growth of sulphate reducing bacteria. Based on methods from sulphate reduction experiments at other mine sites (Blowes et al., 1995; Waybrant et al., 1997), the permeability can be obtained with a matrix of coarse gravel, and the growth of sulphate reducing bacteria may be promoted by the addition of a suitable organic substrate (Waybrant, 1995). At Mount Pleasant, the material used to fill the columns was a mixture of crushed limestone from the Greymount Quarry in Havelock, NB, pea gravel from the Diamond Quarry in Fredericton, fish- and wood-waste compost from St. George, NB (to provide the organic substrate for the bacteria), and creek mud from a marshy area near the Mount Pleasant Mine. Additional creek mud from a swampy area at the Fire Road coal mine near Minto was added later. The creek mud, collected from organic-rich anaerobic sediments was used as a source of sulphate-reducing bacteria. The material was mixed 3:1, gravel to compost, with the gravel composed of 2 ½ parts pea gravel and 0.5 part limestone. The Creek mud was mixed in with a small amount of gypsum ($CaSO_4 \bullet 2H_2O$), a natural source of sulphate added to encourage the establishment of sulphate-reducing conditions.

2.2 Column Setup

Five lengths of 10 cm diameter sewer pipe (4 x 3.33 m long and 1 x 2.56 m long) were mounted vertically, side by side on a workbench. After filling the columns with the

gravel/compost mixture, end caps were put in place and connected in series by 1.25 cm plastic pipe in order to conduct the water along a total flow path within the columns of 19.9 m.

Polyethylene tubing (½" id) was extended from the mine portal to the building containing the columns. Heat tape was attached to the side of the polyethylene (PE) tubing, and then the tubing/heat tape assembly was covered along the entire length by 1 1/4" ABS pipe to retain heat and protect the PE water line. Where possible, the water line was then buried in the ground to prevent freezing. Inside the building, a heavy canvas tent was erected around the columns to help keep the area warm and dry. Before the columns were filled with water, they were purged with CO_2 gas to displace oxygen. Water was then pumped from the mine portal into the columns.

2.3 Sampling and Analytical Methods

The first day of sampling was on November 22, 2001. Samples of the mine water were collected at the outlet of the pump, and then samples were collected at five locations along the length of the columns. Measurements of pH and E_H were made in a sealed flow-through cell. Samples were filtered with 0.45 µm cellulose acetate filters and were split into two sub-samples. One of the sub-samples was acidified, and the other was left unacidified. The samples were refrigerated until they were analyzed. Alkalinity determinations were made on all samples with 25- to 100-mL sub-samples using a Hach Chemical Company digital titrator. Sampling was done every week except in several cases when the experiment was interrupted by frozen water lines.

Major and trace cation analyses were conducted by inductively-coupled plasma optical-emission spectrometry (ICP-OES). Major anions were determined by ion chromatography.

3. Results and Discussion

The results of geochemical sampling are presented in Table 1 and Figures 1a-g. The data are presented for important parameters as a time series, where t_0 represents the first sampling event on Nov. 22, 2001. At each measurement time, the changes that occur in the water chemistry across the length of the column are represented by the difference in the measurements between the inlet and the outlet.

Table 1. Data for chemical parameters measured in the field.

pH versus distance through the columns

Temp		10	15	17	8	7	6	0	15	10	18	6
Time		0	8	16	25	30	36	43	49	56	63	70
Date	Distance (m)	Nov22/01	Nov30/01	Dec6/01	Dec17/01	Dec22/01	Dec28/01	Jan4/02	Jan10/02	Jan17/02	Jan24/02	Jan31/02
tap#1	0	6.13	5.98	5.78	4.81	6.51	6.44	6.26	6.08	6.33	6.2	6.1
tap#2	3.33	6.53	6.28	5.78	6.51	6.36	6.59	6.68	6.49	6.3	6.3	6.15
tap#3	6.66	6.47	6.32	5.68	6.61	6.47	6.71		6.64	6.93	6.38	6.54
tap#4	9.99	6.32	6.52	6.05	6.64	6.6	6.77		6.49	6.47	6.36	6.67
tap#5	13.29	6.16	6.71	6.43	6.65	6.66	6.89		6.76	6.54	6.63	6.78
tap#6	15.85			6.47	6.69	6.69	6.83		6.78	6.63	6.61	6.46

E_H (mv) versus distance through the columns

Date	Distance (m)	Nov 22/01	Nov 30/01	Dec 6/01	Dec 17/01	Dec 22/01	Dec 28/01	Jan4/02	Jan10/02	Jan17/02	Jan24/02	Jan31/02
tap#1	0	205	171	190	363	348	284	308	287	235	275	265
tap#2	3.33	208	131	203	332	316	313	315	251	193	234	235
tap#3	6.66	160		202	334	357	290		234	165	259	219
tap#4	9.99	291		193	316	320	290		220	354	235	209
tap#5	13.29	320		175	316	305	276		221	138	276	159
Tap# 6	15.85			169	294	322	264		259	137	277	150

Alkalinity (mg/L HCO_3) versus distance through the columns

Date	Distance (m)	Nov 22/01	Nov 30/01	Dec 6/01	Dec 17/01	Dec 22/01	Dec 28/01	Jan4/02	Jan10/02	Jan17/02	Jan24/02	Jan31/02
Tap #1	0	27	20	23	21	19	21	38	20	22	17	17
Tap #2	3.33	162	30	28	23	19	25	51	29	32	29	19
Tap #3	6.66	530	54	35	29	19	27		36	47	35	26
Tap #4	9.99	881	78	38	33	26	37		45	53	40	32
Tap #5	13.29		81	40	19	36	40		46	51	43	35
Tap #6	15.85			42	39	39	42		47	54	42	36

3.1 Sulphate Reduction

The principal geochemical indicator of sulphate reduction is the change in sulphate concentration that occurs between the column inlet and outlet. If the sulphate reduction rate is significant, there will be a measurable decline in the concentration of sulphate across the column. The sulphate concentration data from the column experiment do not display a change between the inlet and outlet, indicating that if sulphate reduction has occurred, the rate is not significant.

There are several possible explanations for the low rate of sulphate reduction:

1. The SRB metabolism is sensitive to temperature, and at temperatures below approximately 5°C they become inactive. The column experiments were started in late November, and although the columns were set up inside a heated tent, on many occasions the temperature in the tent dropped below 5°C and on several occasions the temperature dropped below freezing. The maintenance of a constant temperature above 8-10°C should be suitable for SRB growth, but the temperature fluctuations that have occurred do not allow for the establishment of an active SRB culture in the columns.

2. Despite all attempts to insulate and heat the water lines, there have been several interruptions in flow to the columns due to freezing. In one case in late February, water lines cracked and caused the columns to drain. When this happens, oxygen enters the column and disrupts the anaerobic conditions that are required for SRB growth.

The response of SRB to adverse changes in their environment such as low temperatures or the introduction of oxygen is to transform to a dormant state in which their growth stops.

3.2 pH and Alkalinity

The pH and alkalinity show a consistent increase as the water flows through the columns. Although measurable sulphate reduction has not been observed, other organic-carbon degradation reactions such as fermentation may have contributed CO_2 to the system resulting in an alkalinity increase. The dissolution of limestone ($CaCO_3$) in the columns may also contribute to an increase in alkalinity. The increase in pH is probably related to similar net acid-consuming reactions such as limestone dissolution.

3.3 Iron, Zinc and Arsenic

The Fe concentration in the drainage water is important because in the dissolved ferrous (Fe^{2+}) form it may contribute to acidic drainage when it discharges to the surface, contacts atmospheric oxygen and oxidizes to the ferric (Fe^{3+}) form:

$$Fe^{2+} + {}^{1}/_{4}O_2 + {}^{5}/_{2}H_2O \rightarrow Fe(OH)_3 + 2H^{+} \qquad [4]$$

Although the pH of the water draining from the portal is near neutral, the ferrous iron oxidation reaction would result in acidification of the water and increased metal mobility. It is this reaction that creates a necessity for the present practice of lime addition at Mount Pleasant.

The data from the column experiments display a consistent decrease in the Fe concentration. This decrease is very significant because, combined with the observed alkalinity increase, it results in a net decrease in the acid-generating capacity of the water. The mechanism that causes the reduction in the ferrous iron concentration is not yet clear, but it is likely that the increase in alkalinity causes the system to reach saturation with respect to siderite ($FeCO_3$), resulting in siderite precipitation and removal of iron from the water. It is also possible that the iron is removed from solution by ion exchange reactions that occur in the column.

Similar to iron, the zinc concentration decreases across the columns consistently through time. The decrease in the zinc concentration is much less than would be expected if sulphate reduction was occurring in the columns, however, the observed decrease of 30 to 40% is a positive change.

With the exception of the sampling event at day 43, the arsenic concentration in the inlet water is quite uniform between 3 to 5 mg/L. There is not a great difference observed between the inlet and outlet concentrations, although the concentration in the outlet water is quite erratic. Dissolved arsenic occurs in the (III) and (V) oxidation states and its

concentration in the columns is influenced by redox reactions, as well as ion-exchange and precipitation reactions. The redox reactions are likely to have a significant influence on the arsenic mobility in the columns, and the rates of these reactions will be a function of temperature, which may explain the erratic concentration in the outlet solution.

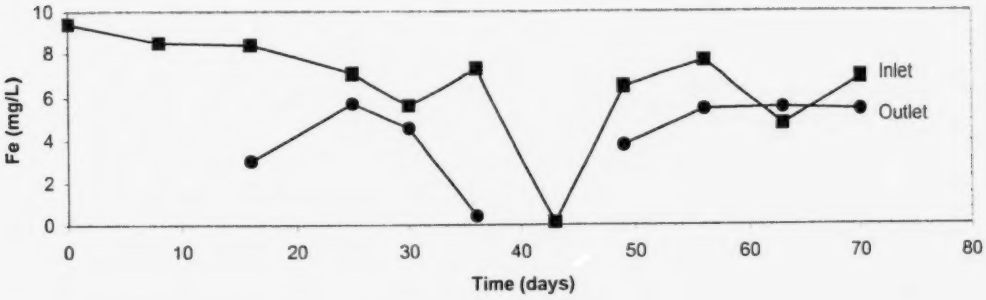

Figure 1a. Iron concentration in columns over time.

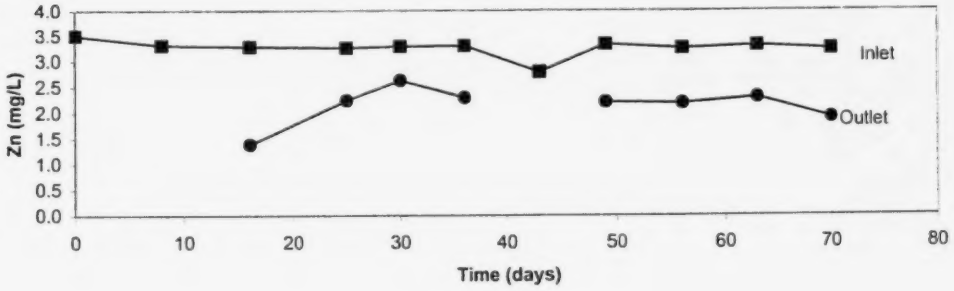

Figure 1b. Zinc concentration in columns over time.

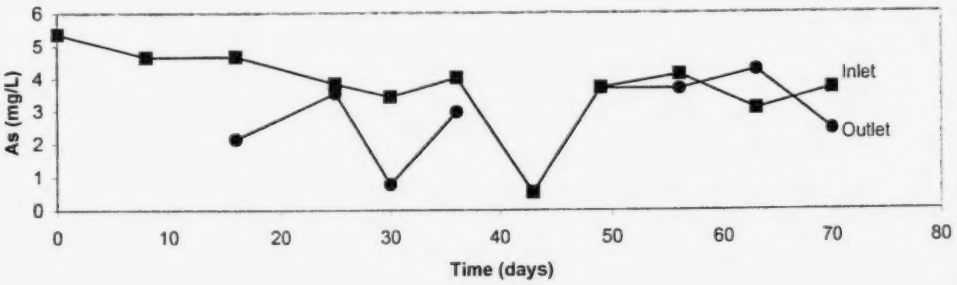

Figure 1c. Arsenic concentration in columns over time.

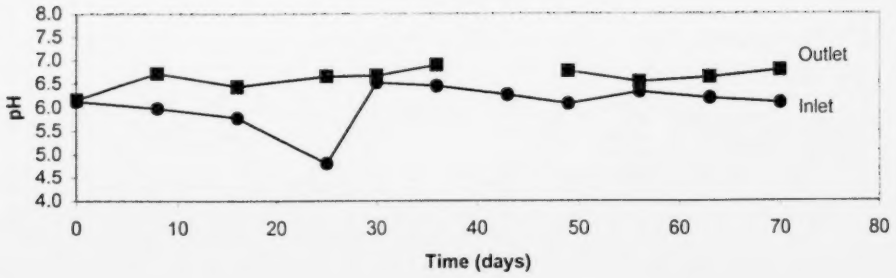

Figure 1d. pH in columns over time.

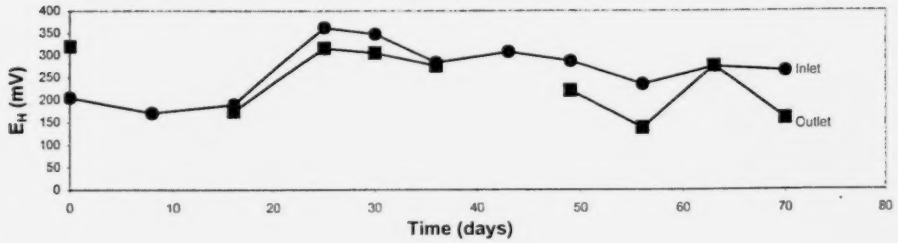

Figure 1e. EH in columns over time.

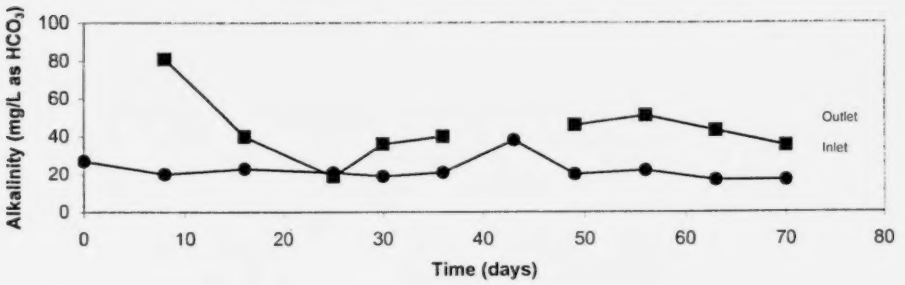

Figure 1f. Alkalinity (mg/L as HCO_3) in columns over time.

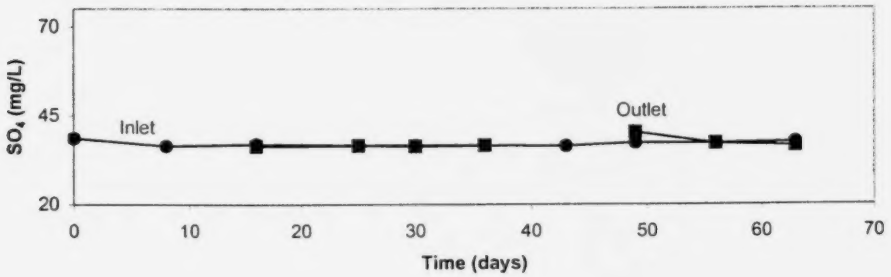

Figure 1g. Sulphate concentration in columns over time.

4. Conclusions

Based on the results of the column experiments, the following conclusions can be made:

- Sulphate reducing conditions have not been attained within the columns because the temperature has fluctuated significantly, commonly declining below 5oC, and occasionally below 0oC. In addition to the low temperatures, frozen and cracked water lines have resulted in oxygen entry into the columns. Both of these conditions prevent the growth and viability of sulphate-reducing bacteria.
- The iron concentration has consistently decreased versus distance through the columns, and the alkalinity concentration has increased. The combination of lower iron and higher alkalinity results in drainage water from the columns with net acid-consuming capacity.
- The zinc concentration has consistently decreased versus distance through the columns, achieving a 30 to 40% decrease relative to the inlet concentration.

5. Recommendation

Despite the efforts to maintain the water flow and a suitable column temperature, the weather conditions through January and February did not allow us to achieve the principal objective which was "to determine the feasibility of bacterially-mediated sulphate (SO_4) reduction as a passive treatment method". Given the level of effort that has gone into the project so far, and the likelihood that warmer temperatures will be attainable in the near future, it is recommended that the experiment continue through the spring and summer in order to develop a full understanding of the potential for sulphate reduction as a water treatment method.

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Appendix I – Geochemical Data

Sample ID	Na	Mg	Al	Si	K	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Pb	Sr	Ca	F	Cl	NO3	SO4
	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/L	mg/L	mg/L	mg/L
N22_1	3.37	0.99	1.52	5.56	2.44	< 0.00	1.29	9.40	0.01	< 0.00	< 0.02	3.51	5.37	< 0.00	< 0.05	0.02	13.02	8.64	2.34	0.09	38.64
N22_2	>	116.80	< 0.04	12.30	57.30	< 0.00	1.04	3.19	< 0.01	0.01	< 0.02	0.06	2.24	< 0.00	< 0.05	> 8.88	> 129.00	0.47	43.87	<0.05	0.37
N22_3	>	128.20	< 0.04	12.98	59.20	< 0.00	0.57	0.66	< 0.01	0.02	< 0.02	0.07	1.86	< 0.00	< 0.05	> 7.74	> 133.10	0.35	0.31	0.06	0.37
N22_4	>	159.10	< 0.04	14.13	39.80	< 0.00	0.61	0.11	< 0.01	0.02	< 0.02	0.05	1.59	< 0.00	< 0.05	> 9.64	> 147.80	0.07	0.51	0.80	0.37
N22_5	>	190.40	< 0.04	15.70	< 0.49	< 0.00	0.85	0.13	< 0.01	0.04	< 0.02	0.06	1.27	< 0.00	< 0.05	> 12.20	> 159.90	0.06	1.83	<0.05	0.37
N30_1	3.45	0.92	1.45	5.48	2.43	< 0.00	1.25	8.49	0.01	< 0.00	< 0.02	3.31	4.67	< 0.00	< 0.05	0.02	12.93	8.59	1.75	<0.05	36.40
N30_2	3.46	> 1.98	0.90	5.47	2.66	< 0.00	0.91	3.81	< 0.01	< 0.00	< 0.02	1.19	3.92	< 0.00	< 0.05	> 0.23	18.78	7.87	1.77	<0.05	37.10
N30_3	4.17	> 3.06	0.30	5.66	4.43	< 0.00	0.90	3.63	< 0.01	< 0.00	< 0.02	0.76	6.50	< 0.00	< 0.05	> 0.35	23.43	6.71	1.80	<0.05	44.28
N30_4	5.05	> 3.84	0.24	5.95	5.45	< 0.00	0.97	3.24	< 0.01	< 0.00	< 0.02	0.62	8.29	< 0.00	< 0.05	> 0.45	27.79	6.06	1.83	<0.05	48.50
N30_5	6.53	> 4.84	0.24	6.69	6.98	< 0.00	1.07	2.37	< 0.01	< 0.00	< 0.02	0.53	8.40	< 0.00	< 0.05	> 0.57	33.38	5.55	0.19	0.31	54.85
D6_1	4.48	0.91	1.39	5.43	2.18	< 0.00	1.23	8.39	0.01	< 0.00	< 0.02	3.28	4.69	< 0.00	< 0.05	0.02	13.02	8.54	1.81	<0.05	36.89
D6_2	4.71	1.03	1.39	5.39	2.19	< 0.00	1.20	3.27	0.01	< 0.00	< 0.02	2.73	2.65	< 0.00	< 0.05	0.06	16.90	8.51	1.78	<0.05	36.92
D6_3	4.01	1.03	1.42	5.41	2.16	< 0.00	1.21	3.01	0.01	< 0.00	< 0.02	2.61	2.41	< 0.00	< 0.05	0.08	18.87	8.38	1.78	<0.05	36.67
D6_4	4.71	1.11	1.34	5.41	2.27	< 0.00	1.21	3.12	< 0.01	< 0.00	< 0.02	2.20	2.20	< 0.00	< 0.05	0.11	20.25	8.38	1.79	<0.05	36.39
D6_5	4.70	1.16	1.24	5.42	2.28	< 0.00	1.20	3.11	< 0.01	< 0.00	< 0.02	1.73	2.15	< 0.00	< 0.05	> 0.14	20.80	8.35	1.77	<0.05	36.37
D6_6	4.75	- 1.21	1.16	5.40	2.29	< 0.00	1.18	3.06	< 0.01	< 0.00	< 0.02	1.39	2.15	< 0.00	< 0.05	> 0.17	21.02	8.31	1.78	<0.05	36.30
D17_1	3.37	0.89	1.47	5.35	2.29	< 0.00	1.23	7.05	0.01	< 0.00	< 0.02	3.26	3.84	< 0.00	< 0.05	0.02	12.84	8.47	1.77	<0.05	36.60
D17_2	3.34	0.92	1.49	5.34	2.29	< 0.00	1.23	6.31	0.01	< 0.00	< 0.02	3.12	3.63	< 0.00	< 0.05	0.03	14.60	8.42	1.80	<0.05	36.62
D17_3	3.38	0.97	1.51	5.34	2.43	< 0.00	1.23	6.05	0.01	< 0.00	< 0.02	2.97	3.57	< 0.00	< 0.05	0.05	16.70	8.40	1.82	<0.05	36.54
D17_4	3.40	1.01	1.50	5.37	2.35	< 0.00	1.25	5.88	0.01	< 0.00	< 0.02	2.77	3.52	< 0.00	< 0.05	0.07	17.73	8.34	1.78	<0.05	36.32
D17_5	3.39	1.06	1.47	5.39	2.31	< 0.00	1.25	5.83	0.01	< 0.00	< 0.02	2.50	3.58	< 0.00	< 0.05	0.09	18.37	8.35	1.77	<0.05	36.51
D17_6	3.49	1.08	1.44	5.33	2.28	< 0.00	1.25	5.72	0.01	< 0.00	< 0.02	2.25	3.55	< 0.00	< 0.05	0.10	18.51	8.34	1.79	<0.05	36.50
D22_1	3.23	0.90	1.49	5.34	2.18	< 0.00	1.22	5.63	0.01	< 0.00	< 0.02	3.29	3.44	< 0.00	< 0.05	0.02	12.63	8.45	1.78	<0.05	36.58
D22_2	3.36	0.96	1.58	5.29	2.28	< 0.00	1.18	0.96	< 0.01	< 0.00	< 0.02	2.95	0.34	< 0.00	< 0.05	0.03	15.51	8.45	1.78	<0.05	36.64
D22_3	3.37	0.99	1.59	5.31	2.30	< 0.00	1.17	2.38	< 0.01	< 0.00	< 0.02	2.86	0.45	< 0.00	< 0.05	0.04	17.44	8.40	1.77	<0.05	36.61
D22_4	3.43	1.01	1.58	5.34	2.33	< 0.00	1.20	3.39	< 0.01	< 0.00	< 0.02	2.79	0.56	< 0.00	< 0.05	0.05	18.62	8.28	1.82	<0.05	36.49
D22_5	3.47	1.02	1.54	5.31	2.33	< 0.00	1.21	4.14	< 0.01	< 0.00	< 0.02	2.69	0.69	< 0.00	< 0.05	0.07	19.55	8.26	1.79	<0.05	36.39
D22_6	3.45	1.04	1.50	5.33	2.35	< 0.00	1.23	4.57	0.01	< 0.00	< 0.02	2.63	0.79	< 0.00	< 0.05	0.07	19.87	8.22	1.82	<0.05	36.30
D28_1	3.27	0.89	1.47	5.39	2.24	< 0.00	1.24	7.26	0.01	< 0.00	< 0.02	3.30	4.03	< 0.00	< 0.05	0.02	12.66	8.44	1.81	<0.05	36.56
D28_2	3.28	0.94	1.49	5.34	2.24	< 0.00	1.26	4.49	0.01	< 0.00	< 0.02	3.17	3.26	< 0.00	< 0.05	0.03	15.03	8.39	1.79	<0.05	36.36
D28_3	4.81	0.97	1.40	5.33	2.12	< 0.00	1.26	2.97	0.01	< 0.00	< 0.02	3.07	3.05	< 0.00	< 0.05	0.04	17.58	8.45	1.79	<0.05	36.75
D28_4	3.36	1.00	1.56	5.40	2.25	< 0.00	1.28	1.77	0.01	< 0.00	< 0.02	2.90	3.00	< 0.00	< 0.05	0.06	19.38	8.51	1.80	<0.05	36.58
D28_5	3.47	1.03	1.54	5.34	2.27	< 0.00	1.26	0.85	< 0.01	< 0.00	< 0.02	2.58	2.96	< 0.00	< 0.05	0.07	21.66	8.50	1.78	<0.05	36.52
D28_6	3.42	1.06	1.49	5.40	2.27	< 0.00	1.25	0.43	< 0.01	< 0.00	< 0.02	2.30	2.97	< 0.00	< 0.05	0.08	22.88	8.54	1.77	<0.05	36.56

Sample ID	Na	Mg	Al	Si	K	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Pb	Sr	Ca	F	Cl	NO3	SO4
	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/L	mg/L	mg/L	mg/L
J10_1	4.42	0.90	1.38	5.38	2.14	< 0.00	1.22	6.48	0.01	< 0.00	< 0.02	3.33	3.72	< 0.00	< 0.05	0.02	13.00	8.47	2.13	<0.05	37.33
J10_2	4.53	0.96	1.31	5.34	2.17	< 0.00	1.23	5.13	0.01	< 0.00	< 0.02	3.09	3.32	< 0.00	< 0.05	0.03	16.19	8.46	2.15	0.09	37.47
J10_3	3.45	0.97	1.31	5.32	2.36	< 0.00	1.23	4.81	0.01	< 0.00	< 0.02	2.78	3.43	< 0.00	< 0.05	0.04	18.38	8.39	2.13	<0.05	40.63
J10_4	3.59	1.03	1.17	5.37	2.45	< 0.00	1.26	4.40	0.01	< 0.00	< 0.02	2.61	3.55	< 0.00	< 0.05	0.06	20.57	8.43	2.12	<0.05	40.71
J10_5	3.49	1.05	1.07	5.41	2.47	< 0.00	1.28	4.07	0.01	< 0.00	< 0.02	2.38	3.68	< 0.00	< 0.05	0.08	21.27	8.47	2.22	<0.05	40.87
J10_6	3.65	1.07	1.03	5.37	2.52	< 0.00	1.28	3.79	0.01	< 0.00	< 0.02	2.21	3.70	< 0.00	< 0.05	0.08	21.95	8.51	2.39	0.06	40.26
J17_1	4.49	0.89	1.36	5.34	2.06	< 0.00	1.22	7.63	< 0.01	< 0.00	< 0.02	3.25	4.12	< 0.00	< 0.05	0.02	12.83	8.42	2.15	<0.05	37.27
J17_2	4.55	1.00	1.20	5.30	2.15	< 0.00	1.21	3.65	< 0.01	< 0.00	< 0.02	2.71	2.14	< 0.00	< 0.05	0.04	18.92	8.41	2.10	<0.05	37.31
J17_3	4.59	1.13	0.93	5.27	2.18	< 0.00	1.28	4.47	0.01	< 0.00	< 0.02	2.51	2.77	< 0.00	< 0.05	0.06	22.26	8.26	2.12	<0.05	37.09
J17_4	3.54	1.20	0.90	5.29	2.30	< 0.00	1.34	5.32	0.01	< 0.00	< 0.02	2.42	3.32	< 0.00	< 0.05	0.08	23.28	8.24	2.47	<0.05	40.59
J17_5	4.73	- 1.23	0.76	5.28	2.18	< 0.00	1.34	5.30	0.01	< 0.00	< 0.02	2.17	3.46	< 0.00	< 0.05	0.09	23.48	8.12	2.07	<0.05	36.95
J17_6	4.78	- 1.29	0.76	5.26	2.20	< 0.00	1.41	5.45	0.01	< 0.00	< 0.02	2.19	3.69	< 0.00	< 0.05	0.10	23.79	8.17	2.16	<0.05	37.15
J24_1	4.50	0.91	1.37	5.31	2.09	< 0.00	1.22	4.75	0.01	< 0.00	< 0.02	3.31	3.07	< 0.00	< 0.05	0.02	12.91	8.50	2.13	<0.05	37.59
J24_2	4.58	1.07	1.22	5.36	2.19	< 0.00	1.24	5.71	0.01	< 0.00	< 0.02	2.89	3.57	< 0.00	< 0.05	0.03	17.57	8.44	2.19	<0.05	39.26
J24_3	4.77	1.06	1.01	5.34	2.32	< 0.00	1.26	5.56	0.01	< 0.00	< 0.02	2.56	3.88	< 0.00	< 0.05	0.05	19.66	8.46	2.17	<0.05	37.82
J24_4	4.78	> 1.45	0.89	5.37	2.42	< 0.00	1.32	5.58	0.01	< 0.00	< 0.02	2.38	4.12	< 0.00	< 0.05	0.06	22.64	8.37	2.17	<0.05	41.36
J24_5	4.98	- 1.31	0.88	5.35	2.45	< 0.00	1.28	5.56	0.01	< 0.00	< 0.02	2.29	4.22	< 0.00	< 0.05	0.07	21.96	8.39	2.16	<0.05	40.42
J24_6	4.85	1.12	0.95	5.38	2.52	< 0.00	1.28	5.51	0.01	< 0.00	< 0.02	2.30	4.27	< 0.00	< 0.05	0.07	21.30	8.41	2.17	<0.05	36.48
J31_1	4.40	0.91	1.37	5.35	2.07	< 0.00	1.23	6.87	0.01	< 0.00	< 0.02	3.23	3.70	< 0.00	< 0.05	0.02	12.91				
J31_2	4.57	0.93	1.39	5.32	2.14	< 0.00	1.21	3.85	0.01	< 0.00	< 0.02	3.14	2.19	< 0.00	< 0.05	0.03	15.03				
J31_3	4.40	0.94	1.42	5.34	2.08	< 0.00	1.20	3.98	0.01	< 0.00	< 0.02	2.94	2.15	< 0.00	< 0.05	0.04	16.53				
J31_4	4.48	0.98	1.34	5.32	2.05	< 0.00	1.19	4.45	< 0.01	< 0.00	< 0.02	2.64	2.19	< 0.00	< 0.05	0.05	17.92				
J31_5	4.49	1.05	1.16	5.32	1.92	< 0.00	1.20	5.12	0.01	< 0.00	< 0.02	2.13	2.32	< 0.00	< 0.05	0.06	19.28				
J31_6	4.51	1.05	1.00	5.34	1.87	< 0.00	1.21	5.39	< 0.01	< 0.00	< 0.02	1.91	2.43	< 0.00	< 0.05	0.07	20.01				

Sulphate-reduction Water Treatment at Mount Pleasant:

Phase II

Passive Treatment of Mine Drainage using Sulphate-reducing Bacteria: A Field Experiment.

Nicolette Stanley and
Tom A. Al. PhD, P.Geo.

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Summary

The research was based at the Mount Pleasant Mine site in southern New Brunswick where Fe, Zn and As-contaminated water drains from the mine portal. The project involves the use of bacterial sulphate reduction to precipitate metals from the water as insoluble metal-sulphide minerals in anaerobic columns. The columns were filled with a permeable reactive mixture that would promote the growth of sulphate-reducing bacteria (SRB). Water samples were collected at six points along the 16 m column flow path, and analysed for the concentrations of major cations , anions, and trace metals, as well as, pH, Eh and alkalinity.

The data suggest that sulphate-reducing conditions have been attained intermittently within the columns. During these time periods the SO_4 concentration decreased by between 30 and 70 %. With the onset of sulphate reduction, a decrease in Fe, Zn, and As was not immediately achieved as might be expected. Instead, during the first few intervals of sulphate-reduction, the concentration of Fe increased from approximately 10 mg/L up to a maximum of 20 mg/L, and the As concentration increased also from 4 mg/L up to a maximum of 70 mg/L. The increases can be attributed to the coexistence of Fe(III)-reducing bacteria and SRB. Prior to the onset of sulphate-reducing conditions, Fe(III) oxy-hydroxides from the mine water accumulated in the columns. As sulphate-reducing conditions were attained in the columns, conditions were also favourable for the reductive dissolution of Fe(III) oxy-hydroxides. These reactions reduce iron to the soluble Fe(II) form, and also mobilize As which is associated with the Fe(III) oxy-hydroxides through adsorption and co-precipitation. After 200 days of running the experiment, the iron concentration started to decrease across the columns from 12 mg/L to 8 mg/L. This is an indication that the SRB were becoming the

predominant microbial colony in the columns and that the excess iron hydroxides have been depleted. During time periods when sulphate reduction was occurring, the concentration of Zn decreased significantly versus distance along the flow path, with initial concentrations of 4.5 mg/L declining as low as 0.1 mg/L.

Because sulphate reduction could only be achieved intermittently, systematic studies of the effects of water residence time, temperature and sulphate concentration could not be completed.

1. Introduction

1.1 Sulphate –reducing bacteria

Sulphate-reducing bacteria (SRB) were discovered in 1895 by a Dutch Biochemist, Beijerinck (Postgate 1984). The SRB were found to be widely distributed, but only active under certain conditions. J.R. Postgate, a professor of Microbiology at the University of Sussex, described them as "Smelly, awkward to grow, intractable to isolate and count, but revealing intriguing novelties of biochemistry and physiology to those persistent enough to stick with them".

The SRB are in a class of dissimilatory sulphate reduction bacteria, which reduce sulphur in the sulphate ion, and bring it from its fully oxidized state to its fully reduced state (Postgate 1984). This is represented by the following reaction:

$$SO_4^{2-} + 2CH_2O \Leftrightarrow H_2S + 2HCO_3^- \qquad [1]$$

Where CH_2O represents a simple form of organic carbon, SO_4 is consumed and hydrogen sulphide gas (H_2S) is produced along with bicarbonate alkalinity. The increase in H_2S enhances the precipitation of metals from solution as metal sulphides:

$$Me^{2+} + H_2S \Leftrightarrow MeS + 2H^+ \qquad [2]$$

Where Me^{2+} represents metals such as Cd, Fe, Ni, Cu, Co, Zn (Waybrant 1995). Combining equations [1] and [2] gives the overall reaction of sulphate reduction and precipitation of metal sulphides:

$$Me^{2+} + SO_4^{2-} + 2CH_2O \rightarrow MeS_{(s)} + 2H_2CO_3^{\circ} \qquad [3]$$

Reaction [1] has been attributed mostly to bacteria called *Desulfibrio sp.* (Tsukamoto and Miller 1999). The two most studied of the genra are *Desulfovibrio* and *Desulfotomaculum,* because they are the easiest to isolate and purify (Ifill 1999). The SRB's are anaerobic bacteria that use simple organic compounds as electron donors for the reduction of sulphate (Gould 1994). They thrive in acidic anaerobic environments and are active up to a pH of 9.5. The presence of SRB with a high metabolic activity is revealed by the blackening of water and sediment due to the precipitation of iron sulphide, and by the smell of H_2S (Ifill 1999).

1.2 Treatment of mine drainage by sulphate reduction

Sulphate-reducing reactions applied in various ways have been studied as a treatment for mine drainage. For example, sulphate-reducing reactions occur in constructed wetlands and were attributed to the neutralization of acid drainage and decreased dissolved metal concentrations (Machemer and Wildeman 1992). Sulphate-reduction reactions have been studied in surface reactors used for treating acid mine drainage derived from coal-mine wastes (Dvorak et al. 1992).

The treatment of mine drainage by SRB is a biogeochemical process that reverses the detrimental effects of sulphide oxidation, and has been studied in field and laboratory settings. Waybrant et al. (1995) studied porous reactive walls that have the potential to remediate mine-tailings impacted groundwater, and to prevent acidic mine drainage and the release of dissolved metals. To achieve this, two acrylic columns were set up and filled with different organic mixtures. Sulphate rich mine-drainage water was pumped through the columns to simulate reactions in a porous reactive barrier. The results from all columns were similar; SO_4 concentrations decreased 500 to 800 $mmol \cdot d^{-1} \cdot m^{-3}$, iron concentrations decreased, and alkalinity increased (Waybrant, 1995; Waybrant et al., 1997). The treatment is due to the ability of the bacteria to reduce SO_4 to sulphide (S^{-2}), which binds with most heavy metals to form insoluble precipitates (equation 2).

When the metals are in this stable solid form they no longer contribute to the contamination of surrounding water systems (Lyew and Sheppard 2001). The metals remain in the system but, when isolated as precipitates they are not a threat to nearby drinking water or aquatic life. If sulphate reduction could be achieved at Mount Pleasant, then it would lead to the passive removal of dissolved metals and SO_4 from the drainage water, and would be accompanied by an increase in alkalinity, and H_2S.

1.3 Background

The research project is located at the Mount Pleasant Mine in southern New Brunswick (Fig 1). Mount Pleasant is a tin (Sn) and tungsten (W) mine that began

production in 1983 and closed in 1985. The deposit contains a variety of metals including W, Sn, zinc (Zn), copper (Cu), and indium (In). Since closing, the mine portal has filled with ground water that contains elevated concentrations of iron (Fe), arsenic (As), and Zn, likely due to the oxidation of pyrite (FeS_2), sphalerite (ZnS), and arsenopyrite (FeAsS) present in the ore body (McCutcheon 2001).

Presently, the mine water flows from the portal at a rate of approximately 140 gal/min (454 L/min) and is treated with lime in an effort to lower the Zn concentration. The lime treatment process requires electrical power, and the maintenance of electrical service at the site is very expensive. Technical evaluation of the lime treatment was done in 1997, and it was determined that the present cost for this method of treatment is $10,000/year and is generally not very efficient (Gilders 1997). Consequently, the New Brunswick Department of Natural Resources and Energy (DNRE-NB) decided to conduct a research program to investigate the potential for establishing a passive treatment system that would not require electrical service. This research was implemented in November 2001 in collaboration with T. Al from the Department of Geology at the University of New Brunswick.

1.4 Objectives

The following objectives were established for the research program:

1. Establish a pilot scale treatment system to promote the growth of sulphate-reducing bacteria to treat the mine effluent.

2. Determine the feasibility of removing metals from the effluent by the precipitation of metal sulphides.
3. Determine the residence time for water in the system that is required to obtain satisfactory water treatment.
4. Identify the precipitates in the suspended solids collected from the column material.

Figure 1. Map of Mount Pleasant

8. Experimental methods

To test the treatment of the Mount Pleasant mine water with SRB, columns were set up in a building near the mine portal and mine water was pumped through the columns (Figs. 2 and 3) with a peristaltic pump. The columns were used to treat the water because they allow sampling at six different points along the flow path. The flow rate of the water through the columns could be adjusted with the pump to increase or decrease the residence time of the mine water.

8.1 Reactive column mixture

In order to achieve effective treatment, the columns must contain a permeable material that will promote the growth of SRB. Based on methods from sulphate-reduction experiments at other mine sites (Blowes et al., 1995; Waybrant et al., 1997), the permeability can be obtained with a matrix of coarse gravel, and the growth of SRB may be promoted by the addition of a suitable organic substrate (Waybrant, 1995). At Mount Pleasant, the material used to fill the columns was a mixture of crushed limestone from the Greymount Quarry in Havelock, NB, pea gravel from the Diamond Quarry in Fredericton, fish and wood-waste compost from St.George, NB (to provide the organic substrate for the bacteria), and creek mud from a marshy area near the Mount Pleasant Mine. Additional creek mud from a swampy area at the Fire Road coal mine near Minto, NB was added later. The creek mud, collected from organic-rich anaerobic sediments

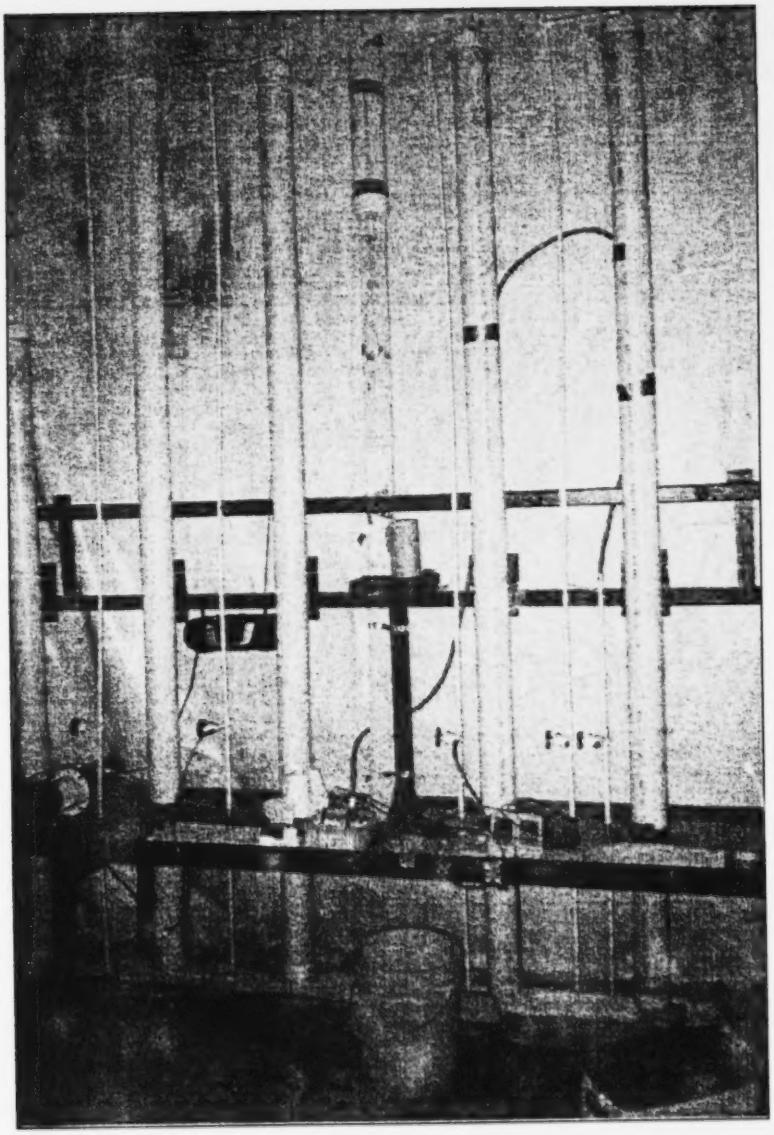

Figure 2. Experimental columns.

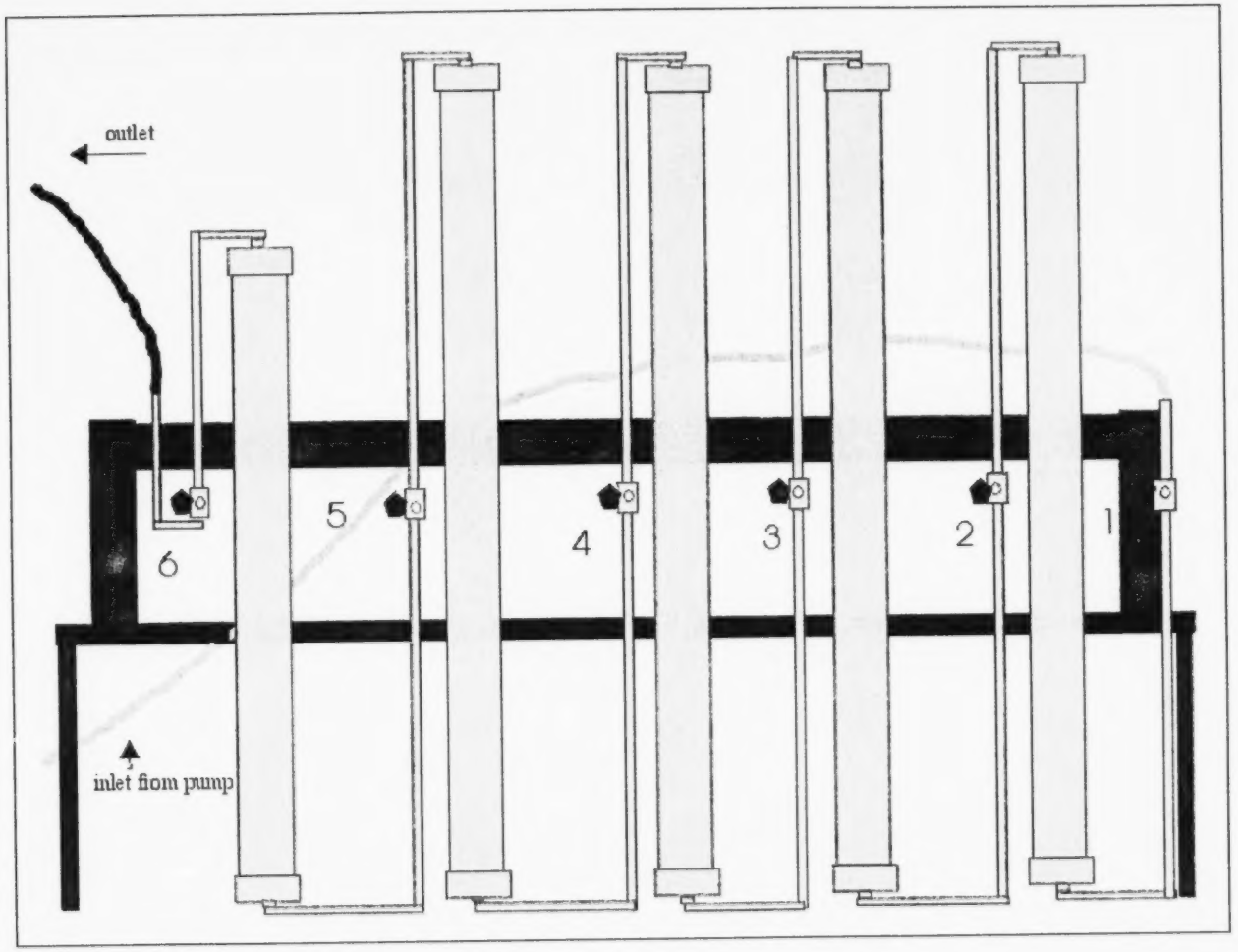

Figure 3. Schematic drawing of columns at Mount Pleasant

was used as a source of SRB. The material was mixed 3:1, gravel to compost, with the gravel composed of 2½ parts pea gravel and ½ part limestone. The Creek mud was mixed in with a small amount of gypsum ($CaSO_4 \bullet 2H_2O$), a natural source of sulphate added to encourage the establishment of sulphate-reducing conditions.

8.2 Column set-up

Five lengths of 10-cm diameter PVC sewer pipe (4 x 3.33 m long and 1 x 2.56 m long) were mounted vertically, side by side on a rack. After filling the columns with the gravel/compost mixture, end caps were put in place and connected in series by 1.25-cm CPVC pipe in order to conduct the water along a total flow path within the columns of 15.9 m.

Polyethylene tubing (½" id) was extended from the mine portal to the building containing the columns. Heat tape was attached to the side of the polyethylene (PE) tubing, and then the tubing/heat tape assembly was covered along the entire length by 1¼" ABS pipe to retain heat and protect the PE water line. Where possible, the water line was buried in the ground to prevent freezing. Inside the building, a heavy canvas tent was erected around the columns to help keep the area warm and dry. Before the columns were filled with water, they were purged with CO_2 gas to displace oxygen. Water was then pumped from the mine portal into the columns.

The amount of water need to fill the columns was measured to determine the porosity inside the columns, 120 L of column material were used to pack the columns and 40 L of water were required to fill the columns, indicating a total porosity of 33.3 %.

3.3 Sampling and analytical methods

The first day of sampling was on November 22, 2001. Samples of the mine water were collected at the column inlet and at five locations along the flow path between each column (Fig. 3). Measurements of pH and E_H were made in a sealed flow-through cell approximately every 1-2 weeks. Measurements of pH were conducted using a Thermo Orion KCl gel-filled combination electrode (model 910600) and Eh measurements were conducted using a Thermo Orion platinum redox electrode (model 96-78-00). Samples were taken with a syringe from a three-way valve on the tap, filtered with 0.45µm cellulose acetate filter membrane, and split into two sub-samples. One of the sub-samples was acidified with trace-metal grade nitric acid, and the other was left unacidified. The samples were refrigerated until they were analyzed. Alkalinity determinations were done colourimetrically in the field with 25 to 100mL filtered sub-samples using a Hach Chemical Company digital titrator and methyl-red bromocresol-green as the indicator. All sample bottles (high density polyethylene) and syringes were acid washed with 5-10% nitric acid prior to use.

Major and trace cation analyses (Be, Na, Mg, Al, Si, K, Cr, Mn, Fe, Co, Cu, Zn, As, Cd, Pb, Sr, Ca, Sb) were conducted by inductively-coupled plasma optical-emission

spectrometry (ICP-OES; Spectro Ciros CCD). The data are included in Appendix I. Major anions (F, Cl, NO_3, PO_4, SO_4) were determined by ion chromatography (IC; Dionex DX-120).

Before sampling the taps, pressure was measured with an oil filled pressure gauge and recorded in pounds per square inch (PSI), and the flow rate of the outlet was measured with a plastic graduated cylinder and recorded in mL/min.

8.4 Postgate's modified medium

To ensure that the SRB have colonized the columns, a growth medium was prepared to detect the presence of the SRB. J.R Postgate has six recipes for biological media used to detect and culture SRB (Postgate 1984). Modifications were made to create a medium suitable for detection of the SRB in the columns (Fortin, pers. com.). The following recipe was used:

Growth medium:

10 g/L tryptone

6 mL/L Na-Lactate (60%)

2 g/L $MgSO_4 \cdot 7H_2O$

0.5 g/L $FeSO_4 \cdot 7H_2O$

0.5 g/L Na_2SO_3

The water was heated on a Thermix in a sterile beaker and the ingredients were added to the boiling water. The pH was adjusted to 7.5 with NaOH and then heated again for 20

minutes. A glass container with a glass stopper was sterilized in the oven and used to store the medium in the fridge.

Reducing Agent:

7.5 mL/L thioglycollic acid

7.5 g/L ascorbic acid

The reducing agent was adjusted to a pH of 7.5. Then, in acid washed and sterile glass test tubes, 1 mL of reducing agent was added to 9 mL of medium. When cooled, 1 mL of sample was added to this, capped immediately and placed in a dark cooler for at least a week. If the test tubes turn black then SRB are present.

9. Results and Discussion

9.1 Aqueous geochemistry

In the Postgate's Media tests for the presence of SRB's, nanopure water was used as a blank and creek sludge from Minto, N.B. was used as a sample that definitely had high levels of SRB. The first trial was unsuccessful, the Minto sample did not turn black neither did the filtered Mount Pleasant samples. The second trial was successful and the Minto sample turned black but the two filtered Mount Pleasant samples did not (Fig. 4). For the third trial the samples from Mount Pleasant were left unfiltered and they were found to contain SRB as did the Minto sample (Fig. 5). This experiment verified that there are SRB in the columns, the results do not provide an indication of the abundance or activity of the SRB present.

The geochemical data are presented for important parameters as time-series graphs (Fig. 6 to 11), where t_0 represents the first sampling event on Nov. 22, 2001. At each measurement time, the changes that occur in the water chemistry across the length of the column are represented by the difference in the measurements between the inlet and the outlet.

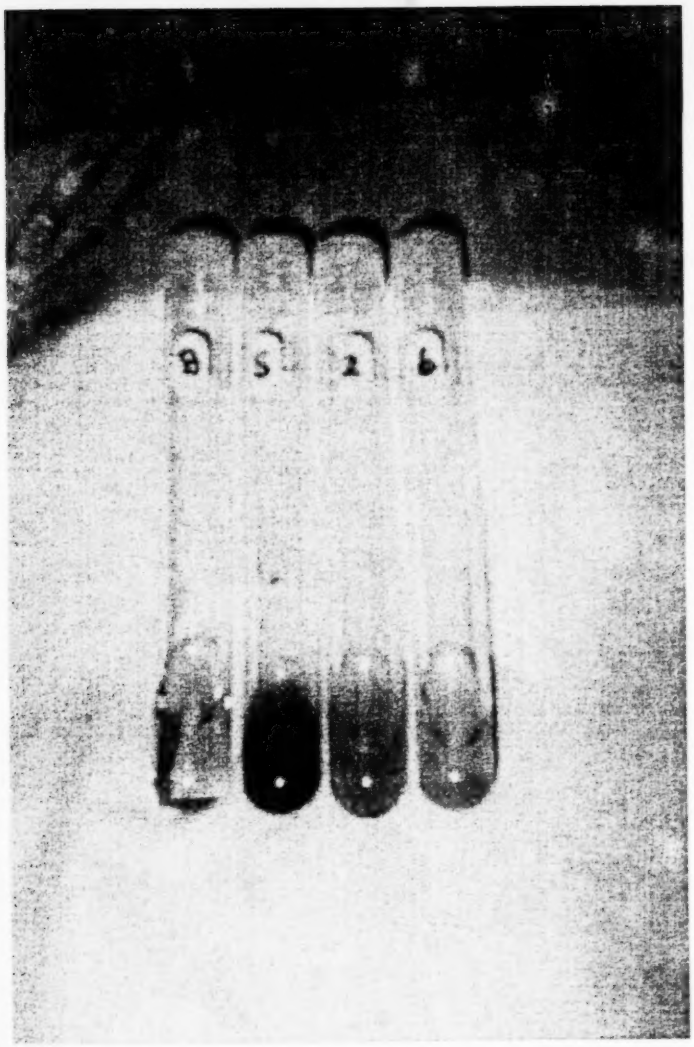

Figure 4. The second experiment, using Postgate's modified medium. From left to right the test tubes have nanopure water (B), Minto sludge water (S), filtered water from tap #2 (water from column #1), and filtered water from tap#6 (water from column #5). The black colour indicates the presence of SRB.

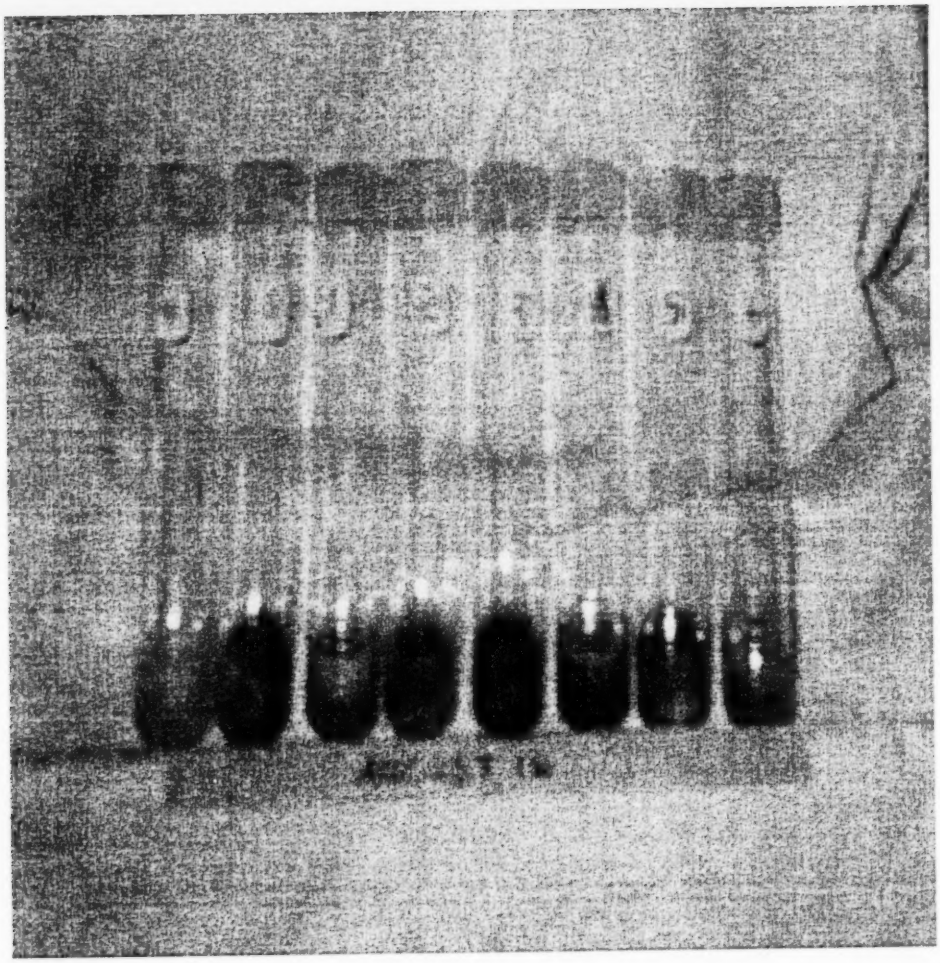

Figure 5. The third experiment, using Postgate's modified medium. From left to right the test tubes contain nanopure water (B), Minto sludge water (S), and unfiltered water from each tap of the experimental columns (inlet (1) to outlet (2)). The black indicated the presence of SRB in every sample but the blank and the inlet water from the mine portal.

If the sulphate-reduction rate is significant, there will be a measurable decline in the concentration of SO_4 across the column. Therefore, the principal geochemical indicator of sulphate reduction is the decrease in total SO_4 concentration that occurs between the column inlet and outlet. Figure 6 shows a graph of the change in SO_4 concentration from inlet to outlet over 268 days of flow. Sulphate reduction occurs intermittently over the sampling period, and during these events the SO_4 concentration decreased by between 30% and 70%. To relate the 5 events of sulphate reduction with the important geochemistry data, the arrows are carried through Figures 6-11. Numerical values for the data shown on Figures 6-11 can be found in Appendix I.

There is a consistent, small increase in pH across the columns (Fig. 7), not exclusively when SO_4 reduction is occurring. The gradual increase in pH can be attributed to a number of different mechanisms. The build up of iron hydroxides in the columns encourages the growth of iron-reducing bacteria. These bacteria reduce the iron hydroxides to soluble Fe(II), and an increase in pH generally results from this reducing reaction (equation 4). The pH is also expected to increase as a result of calcite dissolution (equation 5) in the columns.

$$Fe^{(III)}O(OH)_{(s)} + {}^{1}/_{4}CH_2O + {}^{7}/_{4}H^{+} \rightarrow Fe^{2+} + {}^{1}/_{4}HCO_3^{-} + {}^{3}/_{2}\,H_2O \qquad [4]$$

$$CaCO_3 + H^{+} \rightarrow Ca^{2+} + HCO_3^{-} \qquad [5]$$

The alkalinity data are similar to pH in that even when SO_4 reduction does not occur, there is a small increase in alkalinity across the columns (Fig. 8). Alkalinity is a product of various reduction reactions and similar to the pH changes, the alkalinity increase can be attributed to the reduction of Fe oxy-hydroxides within the columns (equation 4). The alkalinity increase can also be related to the dissolution of calcite (equation 5). When sulphate-reducing conditions are achieved there is a very distinctive, large increase in alkalinity (Fig. 8).

As might be expected when sulphate-reduction occurs, a decrease in Fe and As concentrations was not immediately achieved (Figs. 9 & 10). On the contrary, concentrations of Fe and As actually increased (10 mg Fe/L up to a maximum of 20 mg Fe/L; and 4 mg As/L up to a maximum of 70 mg As/L) during the first few intervals of sulphate-reduction. This can be attributed to competing microbial reactions that may occur in the columns because of the accumulation of iron hydroxides before the SRB could become established. As the excess iron hydroxides are gradually reduced by iron-reducing bacteria, Fe(III) is reduced to soluble Fe(II). Under these conditions, arsenic desorbs from the hydroxide surface and is released into the water. Based on thermodynamic constraints, it is expected that the excess iron hydroxides must be depleted before sulphate-reducing reactions can become effective.

After 200 days of running the experiment, the iron concentration started to decrease across the columns from 12 mg/L to 8 mg/L. This was an indication that the

SRB were becoming the predominant microbial colony in the columns and that the excess iron hydroxides were being depleted.

Zinc concentrations decreased constantly across the columns (Fig. 11) from approximately 3.5 mg/L to about 2 mg/L when sulphate-reduction wasn't occurring. During events of sulphate reduction the decrease was more significant to values as low as 0.1 mg/L. When sulphate reduction wasn't occurring, the decrease in Zn concentrations may be explained by the precipitation of Zn carbonate. The increase in alkalinity creates conditions favourable to the precipitation of carbonate with solubilities lower than calcite. When sulphate reduction occurred, the Zn removal from solution was most effective, probably as a result of the simultaneous precipitation of zinc carbonates and sulphides.

Other geochemical parameters such as Eh, flow rate into the columns, temperature and pressure can be found in Appendix I. Anion and cation concentrations that were not discussed in results can also be found in Appendix I.

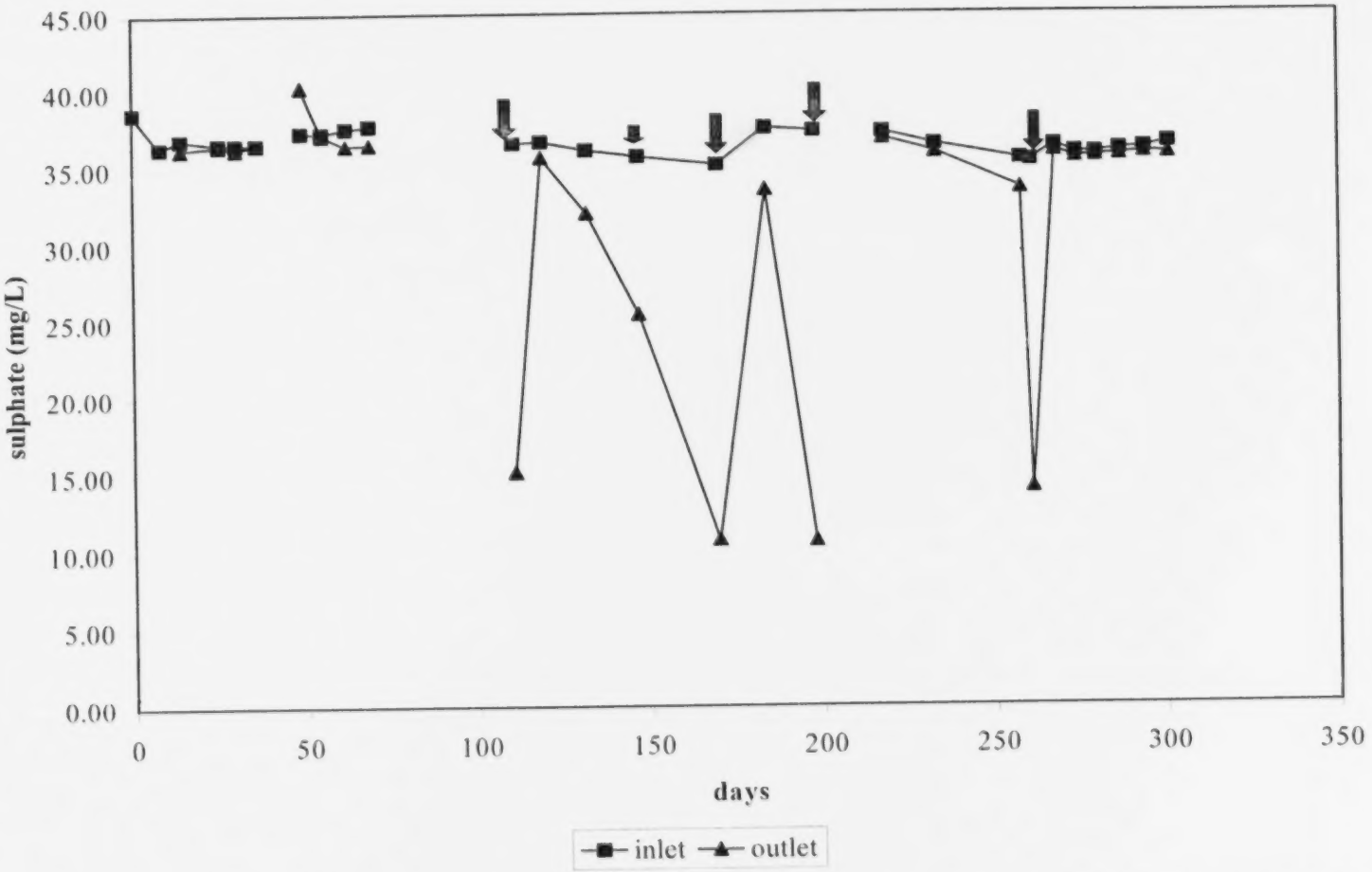

Figure 6. Sulphate concentrations versus time in the column inlet and outlet. Arrows indicate time periods when sulphate reduction occurred.

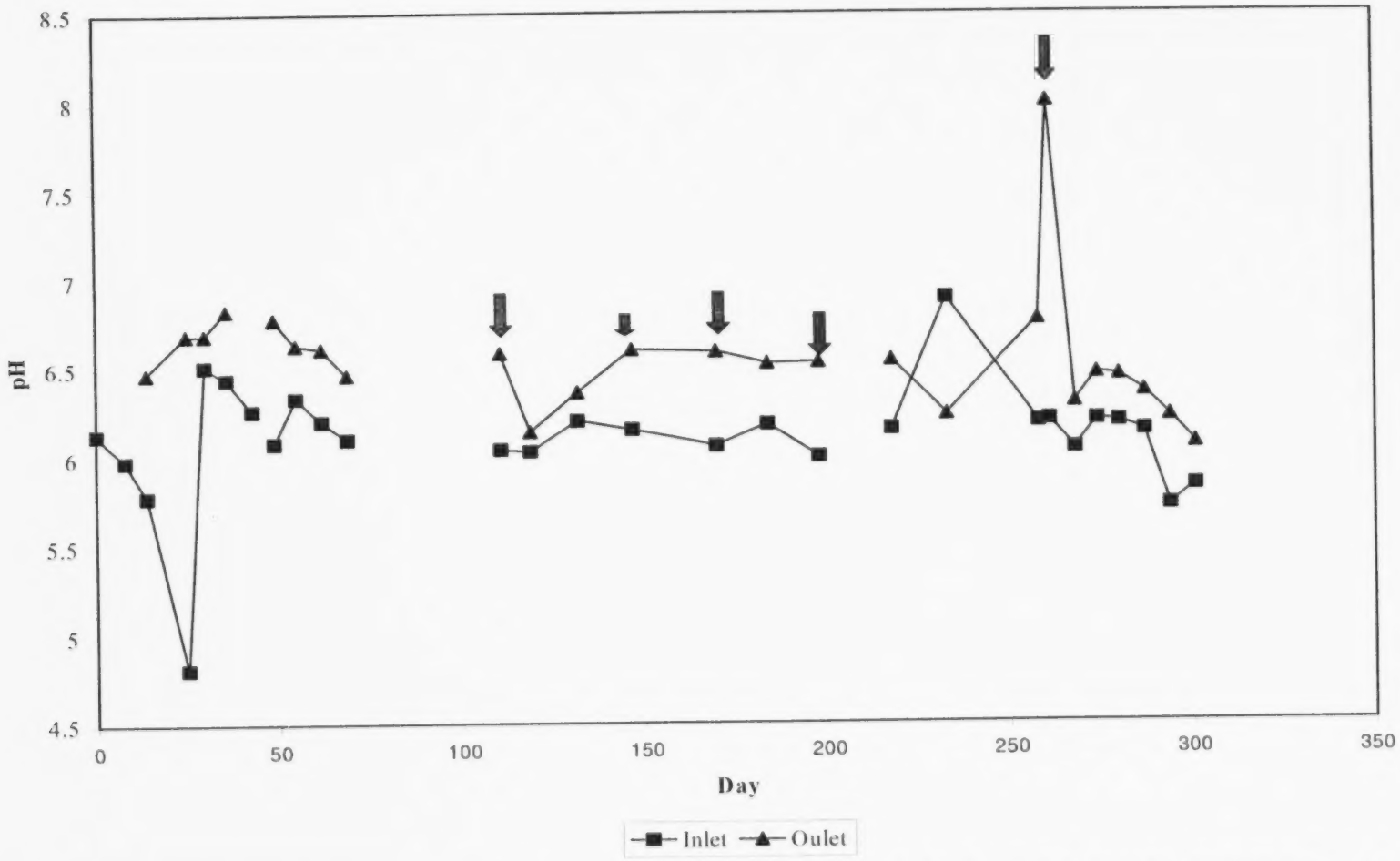

Figure 7. pH versus time in the column inlet and outlet. Arrows indicate time periods when sulphate reduction was occurring.

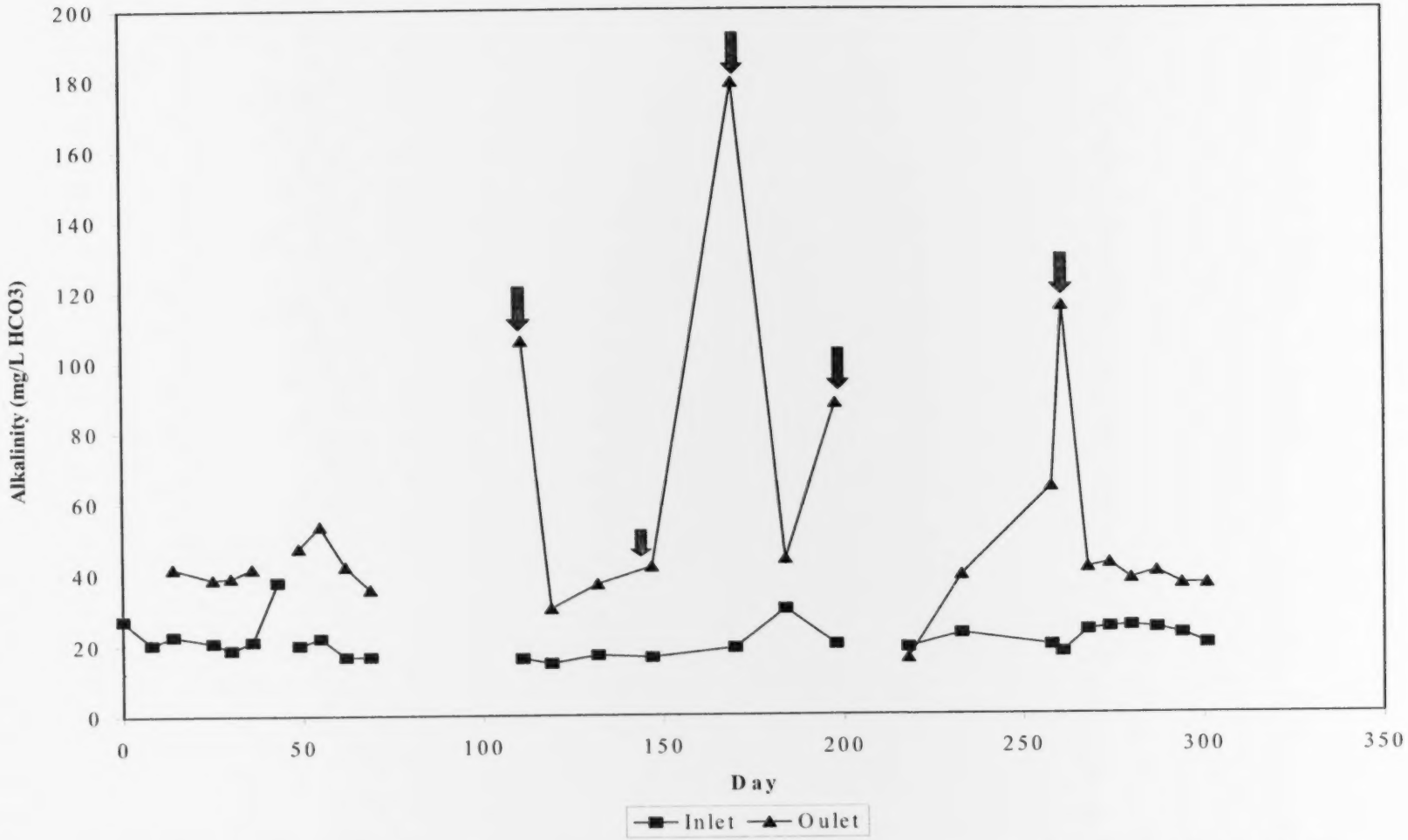

Figure 8. Alkalinity versus time in the column inlet and outlet. Arrows indicate time periods when sulphate reduction occurred.

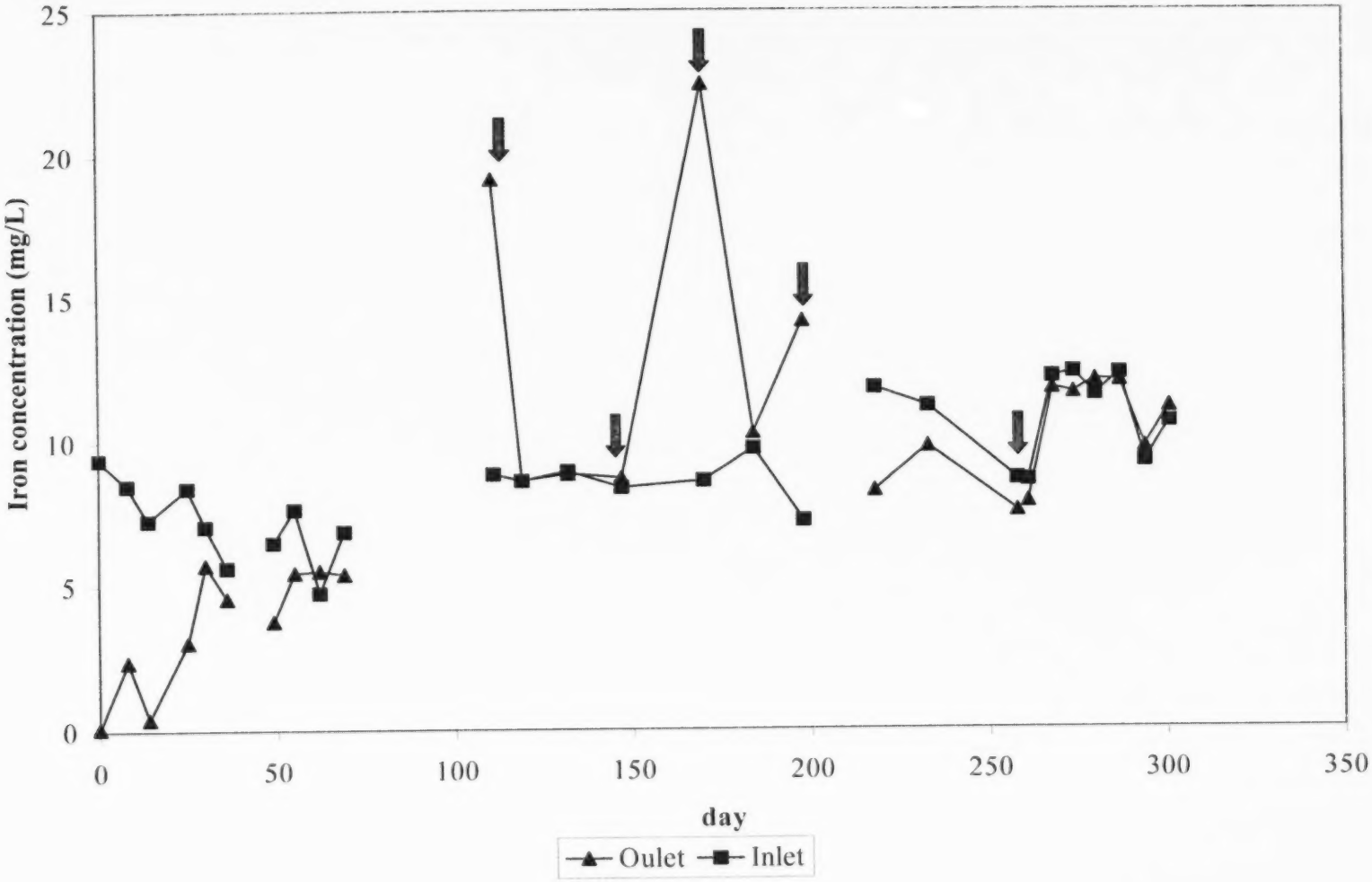

Figure 9. Iron concentrations versus time in the column inlet and outlet. Arrows indicate time periods when sulphate reduction occurred.

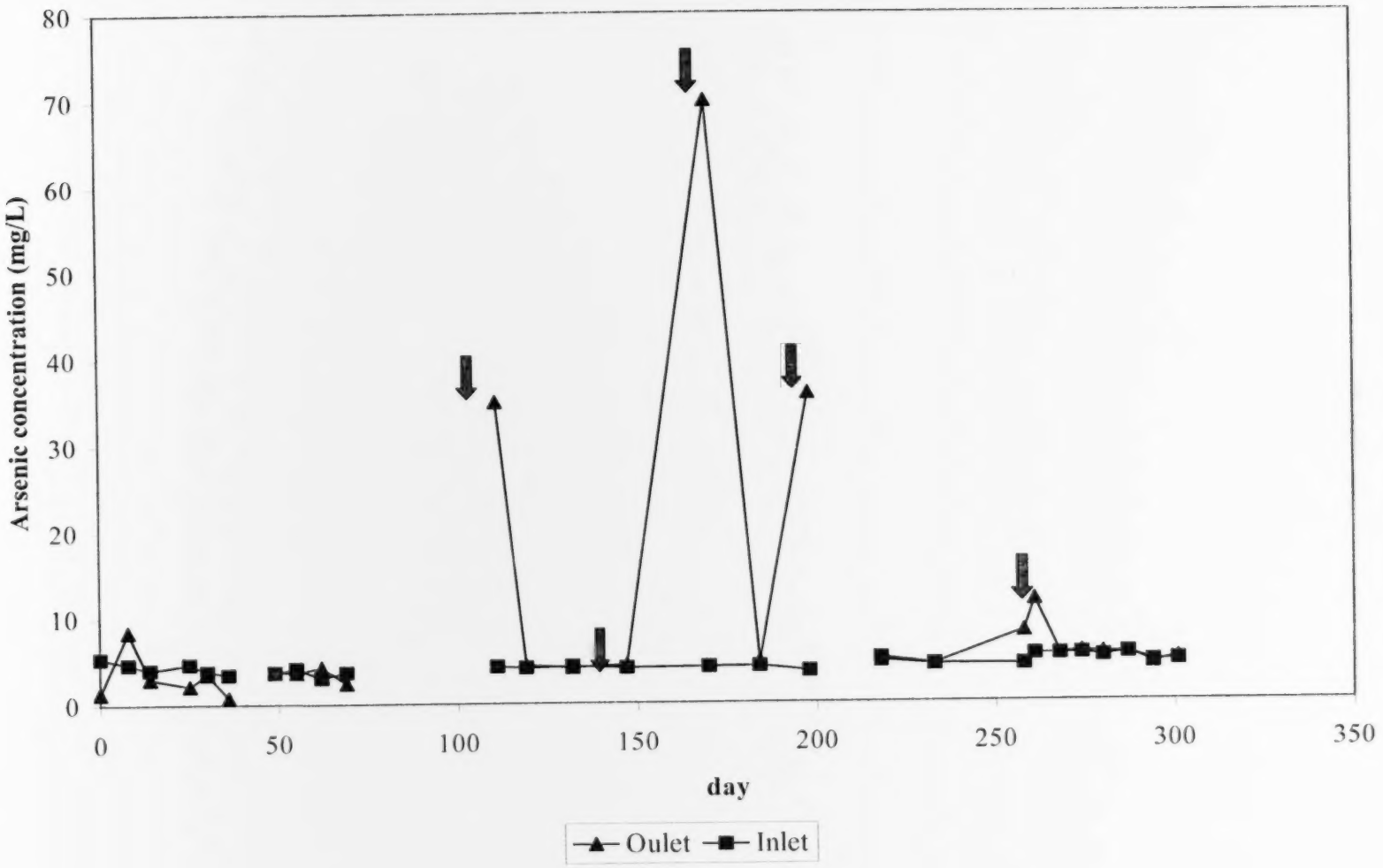

Figure 10. Arsenic concentrations versus time in the column inlet and outlet. Arrows indicate time periods when sulphate reduction occurred.

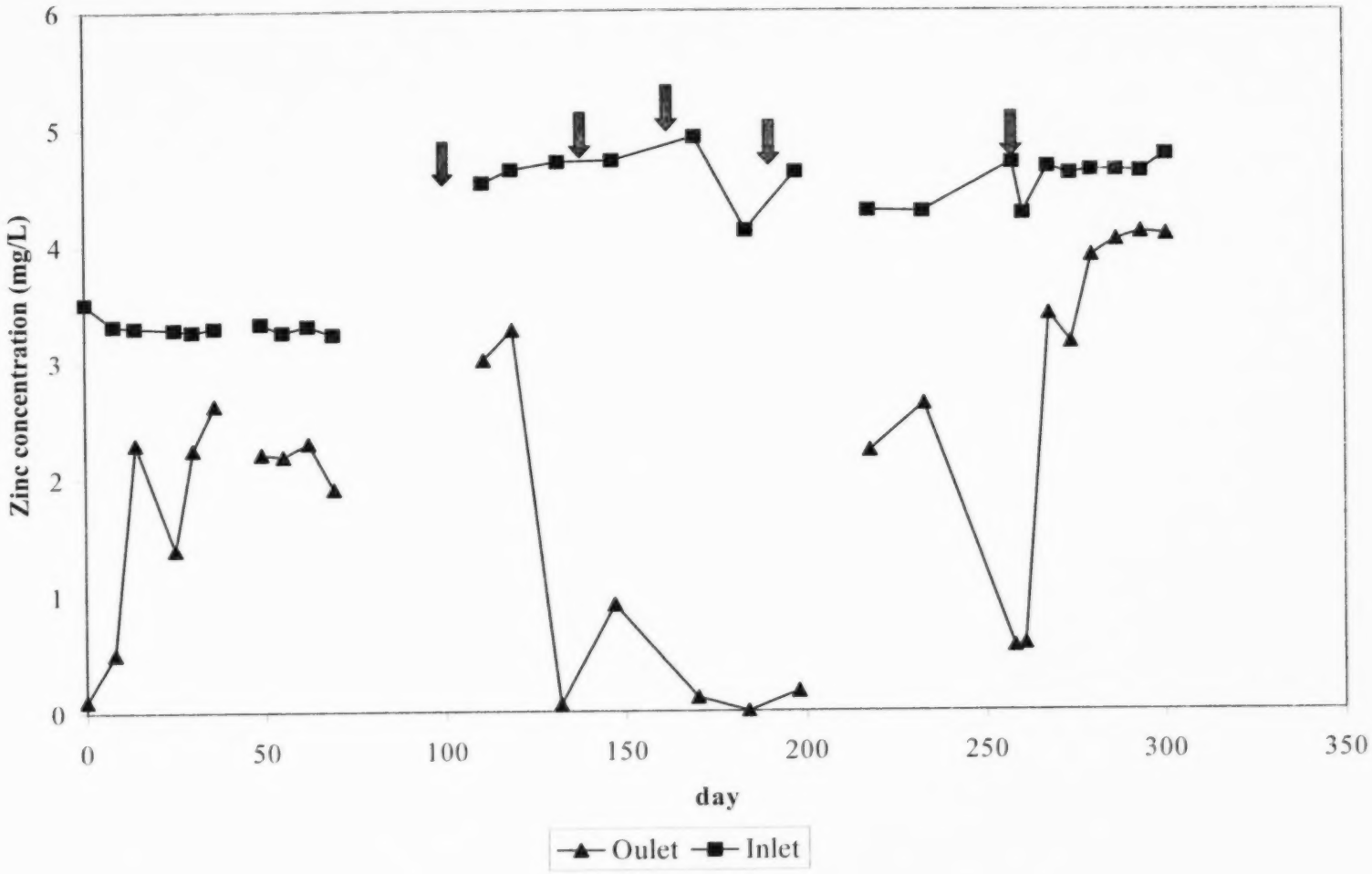

Figure 11. Zinc concentrations versus time in the column inlet and outlet. Arrows indicate time periods when sulphate reduction occurred.

9.2 Hydrogeology

During the course of the experiments, the flow rate through the solumns varied between 0.1 and 0.7 L/min (Fig. 12). As indicated by the arrows in Figure 12, sulphate reduction occurred throughout the range of flow conditions and it is not possible to define a limit on residence time within the columns within which sulphate reduction is possible. The role of residence time in controlling sulphate reduction could not be assessed quantitatively due to the intermittent occurrence of sulphate reduction.

The residence time within the columns is a function of the flow rate and is defined as follows:

Darcy Flux (q) = Q/A

Average Pore Water Velocity (v) = q/n

Residence time (T_R) = L / V

Where:

Q = volumetric flow rate (Fig.12)

D = Diameter of columns = 0.1015 m

A = cross sectional area of column = $\pi r^2 = \pi * (0.05075m)^2 = 8.09 \times 10^{-3} m^2$

n = porosity = 0.33

L = length = 15.9 m

The range of residence times during the course of the experiments are presented in Table 1.

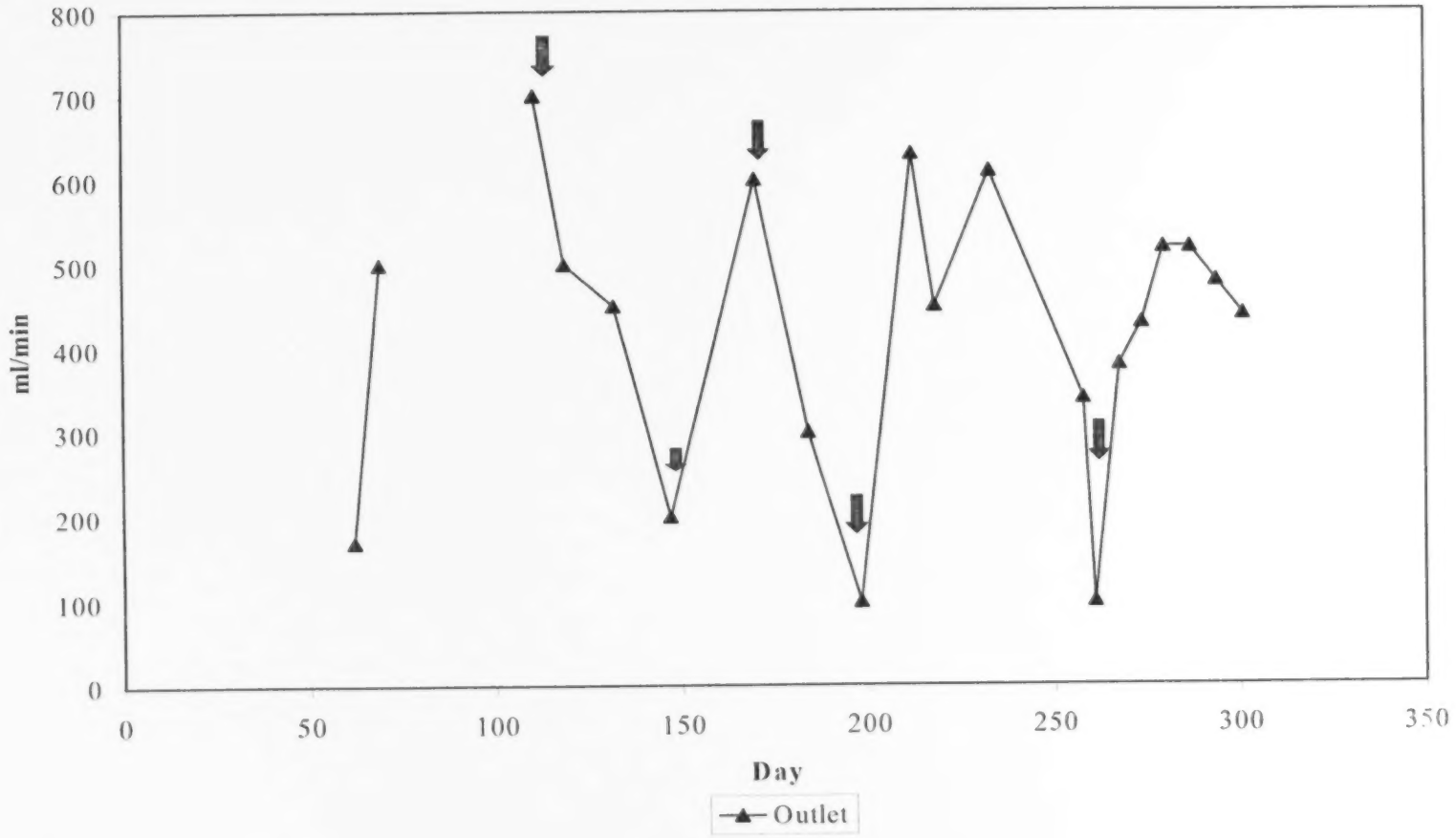

Figure 12. flow rate versus time in the outlet. Arrows indicate time periods when sulphate reduction occurred

Table 1. Average pore water velocity range and residence time in the reactive column material.

	Flow rate (Q) m^3/min	*Flux (q)* *m/min*	*Velocity (V)* *m/min*	T_R *Min*
Max	7×10^{-4}	0.086	0.26	61
Min	1×10^{-4}	0.012	0.036	442

10. Conclusions

Growth of the sulphate-reducing bacteria was achieved in the columns, but not continuously. While sulphate-reducing conditions were maintained the removal of Zn from the mine water was very efficient indicating that that sulphide precipitation is an effective treatment method for dissolved Zn.

Sulphate reduction did not effectively reduce the Fe concentrations in the mine water, probably as a result of the accumulation of Fe(III) hydroxides in the columns in between sulphate-reduction events. These accumulations of Fe(III) hydroxide must be chemically reduced and the Fe removed from the system before effective iron removal is expected. Under conditions of steady-state sulphate reduction it is likely that iron treatment would be effective.

It is uncertain whether efficient As treatment could be attained in the system. The inlet As concentrations are very high and it is likely that a significant amount of the As would remain in a soluble As(III) form.

It was not possible to determine the residence time necessary to obtain steady-state sulphate-reducing conditions due to the intermittent onset of sulphate reduction in the columns.

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Appendix II

day	Sample ID	pH	Eh	alkalinity HCO3 mg/l	Be mg/l	Na mg/l	Mg mg/l	Al mg/l	Si mg/l	K mg/l	Mn mg/l	Fe mg/l	Co mg/l	Ni mg/l	Zn mg/l	As mg/l	Sr mg/l	Ca mg/l	F mg/l	Cl mg/l	NO3 mg/l	SO4 mg/l	flow mL/min	temperature celcius	pressure psi	
0	Nov22_1	6.13	205	27	0.002	3.4	1.0	1.52	5.6	2.4	1.3	9.4	0.011	0.005	3.5	5.4	0.02	13.0	8.6	2.3	0.09	38.6		-	-	-
	Nov22_2	6.53	208	162	0.005	54.3	116.8	0.04	12.3	57.3	1.0	3.2	0.010	0.009	0.1	2.2	8.88	129.0	0.5	43.9	-0.01	0.4				-
	Nov22_3	6.47	160	530	0.005	35.3	128.2	0.04	13.0	59.2	0.6	0.7	0.010	0.016	0.1	1.9	7.74	133.1	0.3	0.3	0.06	0.4				-
	Nov22_4	6.32	291	881	0.005	0.0	159.1	0.04	14.1	39.8	0.6	0.1	0.010	0.022	0.1	1.6	9.64	147.8	0.1	0.5	0.80	0.4				-
	Nov22_5	6.16	320		0.005	0.0	190.4	0.04	15.7	0.5	0.8	0.1	0.010	0.042	0.1	1.3	12.20	159.9	0.1	1.8	-1.20	0.4				-
8	Nov30_1	5.98	171	20	0.002	3.4	0.9	1.45	5.5	2.4	1.2	8.5	0.011	0.005	3.3	4.7	0.02	12.9	8.6	1.8	-0.01	36.4		-	15	-
	Nov30_2	6.28	131	30	0.001	3.5	2.0	0.90	5.5	2.7	0.9	3.8	0.010	0.005	1.2	3.9	0.23	18.8	7.9	1.8	-0.02	37.1				-
	Nov30_3	6.32	0	54	0.005	4.2	3.1	0.30	5.7	4.4	0.9	3.6	0.010	0.005	0.8	6.5	0.35	23.4	6.7	1.8	-0.01	44.3				-
	Nov30_4	6.52	0	78	0.005	5.1	3.8	0.24	6.0	5.5	1.0	3.2	0.010	0.005	0.6	8.3	0.45	27.8	6.1	1.8	-0.03	48.5				-
	Nov30_5	6.71	0	81	0.005	-6.53	4.8	0.24	6.7	7.0	1.1	2.4	0.010	0.005	0.5	8.4	0.57	33.4	5.5	0.2	0.31	54.9				-
14	Dec17_1	5.78	190	23	0.002	3.4	0.9	1.47	5.4	2.3	1.2	7.1	0.012	0.005	3.3	3.8	0.02	12.6	8.5	1.8	-0.01	36.9	280		17	-
	Dec17_2	5.78	203	28	0.002	3.3	0.9	1.49	5.3	2.3	1.2	6.3	0.011	0.005	3.1	3.6	0.03	14.6	8.5	1.8	-0.02	36.9				-
	Dec17_3	5.68	202	35	0.002	3.4	1.0	1.51	5.3	2.4	1.2	6.1	0.011	0.005	3.0	3.6	0.05	16.7	8.4	1.8	-0.03	36.7				-
	Dec17_4	6.05	193	38	0.001	3.4	1.0	1.50	5.4	2.3	1.2	5.9	0.011	0.005	2.8	3.5	0.07	17.7	8.4	1.8	-0.01	36.4				-
	Dec17_5	6.43	175	40	0.001	3.4	1.1	1.47	5.4	2.3	1.3	5.8	0.011	0.005	2.5	3.6	0.09	18.4	8.4	1.8	-0.03	36.4				-
	Dec17_6	6.47	169	42	0.001	3.5	1.1	1.44	5.3	2.3	1.2	5.7	0.011	0.005	2.2	3.5	0.10	18.5	8.3	1.8	-0.02	36.3				-
25	Dec22_1	4.81	363	21	0.002	3.2	0.9	1.49	5.3	2.2	1.2	5.6	0.011	0.005	3.3	3.4	0.02	12.6	8.5	1.8	-0.01	36.6		-	8	-
	Dec22_2	6.51	332	23	0.002	3.4	1.0	1.58	5.3	2.3	1.2	1.0	0.010	0.005	2.9	0.3	0.03	15.5	8.4	1.8	0.00	36.6				-
	Dec22_3	6.61	334	29	0.002	3.4	1.0	1.59	5.3	2.3	1.2	2.4	0.010	0.005	2.9	0.5	0.04	17.4	8.4	1.8	0.01	36.5				-
	Dec22_4	6.64	316	33	0.002	3.4	1.0	1.58	5.3	2.3	1.2	3.4	0.010	0.005	2.8	0.6	0.05	18.6	8.3	1.8	-0.02	36.3				-
	Dec22_5	6.66	316	19	0.002	3.5	1.0	1.54	5.3	2.3	1.2	4.1	0.010	0.005	2.7	0.7	0.07	19.6	8.4	1.8	-0.02	36.5				-
	Dec22_6	6.69	294	39	0.001	3.5	1.0	1.50	5.3	2.4	1.2	4.6	0.011	0.005	2.6	0.8	0.07	19.9	8.3	1.8	-0.02	36.5				-
30	Dec28_1	6.51	348	19	0.002	3.3	0.9	1.47	5.4	2.2	1.2	7.3	0.011	0.005	3.3	4.0	0.02	12.7	8.5	1.8	0.02	36.6		-	7	-
	Dec28_2	6.36	316	19	0.002	3.3	0.9	1.49	5.3	2.2	1.3	4.5	0.011	0.005	3.2	3.3	0.03	15.0	8.5	1.8	-0.02	36.6				-
	Dec28_3	6.47	357	19	0.002	4.8	1.0	1.40	5.3	2.1	1.3	3.0	0.011	0.005	3.1	3.1	0.04	17.6	8.4	1.8	-0.01	36.6				-
	Dec28_4	6.60	320	26	0.002	3.4	1.0	1.56	5.4	2.3	1.3	1.8	0.011	0.005	2.9	3.0	0.06	19.4	8.3	1.8	-0.01	36.5				-
	Dec28_5	6.66	305	36	0.001	3.5	1.0	1.54	5.3	2.3	1.3	0.9	0.010	0.005	2.6	3.0	0.07	21.7	8.3	1.8	-0.03	36.4				-
	Dec28_6	6.69	322	39	0.001	3.4	1.1	1.49	5.4	2.3	1.3	0.4	0.010	0.005	2.3	3.0	0.08	22.9	8.2	1.8	-0.02	36.3				-
36	Dec6_1	6.44	284	21	0.002	4.5	0.9	1.39	5.4	2.2	1.2	8.4	0.011	0.005	3.3	4.7	0.02	13.0	8.4	1.8	-0.01	36.6		-	6	-
	Dec6_2	6.59	313	25	0.002	4.7	1.0	1.39	5.4	2.2	1.2	3.3	0.010	0.005	2.7	2.6	0.06	16.9	8.4	1.8	-0.01	36.4				-
	Dec6_3	6.71	290	27	0.001	4.0	1.0	1.42	5.4	2.2	1.2	3.0	0.010	0.005	2.6	2.4	0.08	18.9	8.5	1.8	0.00	36.8				-
	Dec6_4	6.77	290	37	0.001	4.7	1.1	1.34	5.4	2.3	1.2	3.1	0.010	0.005	2.2	2.2	0.11	20.3	8.5	1.8	-0.01	36.6				-
	Dec6_5	6.89	276	40	0.001	4.7	1.2	1.24	5.4	2.3	1.2	3.1	0.010	0.005	1.7	2.2	0.14	20.8	8.5	1.8	-0.01	36.5				-
	Dec6_6	6.83	264	42	0.001	4.7	-1.206	1.16	5.4	2.3	1.2	3.1	0.010	0.005	1.4	2.2	0.17	21.0	8.5	1.8	-0.02	36.6				-
43	J4_1	6.26	308	38	0.001	4.5	1.1	1.14	5.2	2.0	1.2	0.1	0.010	0.005	2.8	0.5	0.03	19.7	8.3	1.8	-0.02	36.5		-	-	4
	J4_2	6.68	315	51	0.001	4.4	1.2	1.14	5.3	1.9	1.3	0.1	0.010	0.005	2.8	0.3	0.05	22.2	8.0	1.8	-0.01	36.4				4
49	Jan10_1	6.08	287	20	0.002	4.4	0.9	1.38	5.4	2.1	1.2	6.5	0.011	0.006	3.3	3.7	0.02	13.0	8.5	2.1	0.01	37.3	125	15	14	
	Jan10_2	6.49	251	29	0.002	4.6	1.0	1.31	5.3	2.2	1.2	5.1	0.011	0.006	3.1	3.3	0.03	16.2	8.5	2.2	0.09	37.5				14
	Jan10_3	6.64	234	36	0.002	3.5	1.0	1.31	5.3	2.4	1.2	4.8	0.012	0.006	2.8	3.4	0.04	18.4	8.4	2.1	0.04	40.6				14
	Jan10_4	6.49	220	45	0.001	3.6	1.0	1.17	5.4	2.4	1.3	4.4	0.012	0.006	2.6	3.6	0.06	20.6	8.4	2.1	0.03	40.7				14
	Jan10_5	6.76	221	46	0.001	3.6	1.1	1.07	5.4	2.5	1.3	4.1	0.012	0.006	2.4	3.7	0.08	21.3	8.5	2.2	0.03	40.9				11
	Jan10_6	6.78	259	47	0.001	3.6	1.1	1.03	5.4	2.5	1.3	3.8	0.013	0.006	2.2	3.7	0.08	22.0	8.5	2.4	0.06	40.3				2
55	Jan17_1	6.33	235	22	0.002	4.5	0.9	1.36	5.3	2.1	1.2	7.6	0.010	0.006	3.3	4.1	0.02	12.8	8.4	2.2	0.00	37.3			10	15
	Jan17_2	6.30	193	32	0.001	4.6	1.0	1.20	5.3	2.2	1.2	3.7	0.010	0.006	2.7	2.1	0.04	18.9	8.4	2.1	0.01	37.3				14
	Jan17_3	6.93	166	47	0.001	4.6	1.1	0.93	5.3	2.2	1.3	4.5	0.011	0.006	2.5	2.8	0.06	22.3	8.3	2.1	0.01	37.1				14
	Jan17_4	6.47	354	53	0.001	3.5	1.2	0.90	5.3	2.3	1.3	5.3	0.011	0.006	2.4	3.3	0.08	23.3	8.2	2.5	0.01	40.6				13
	Jan17_5	6.54	138	51	0.001	4.7	-1.232	0.76	5.3	2.2	1.3	5.3	0.012	0.006	2.2	3.5	0.09	23.5	8.1	2.1	0.00	37.0				8
	Jan17_6	6.63	137	54	0.001	4.8	-1.291	0.76	5.3	2.2	1.4	5.5	0.013	0.006	2.2	3.7	0.10	23.8	8.2	2.2	0.00	37.2				2
62	Jan24_1	6.20	275	17	0.002	4.5	0.9	1.37	5.3	2.1	1.2	4.8	0.011	0.005	3.3	3.1	0.02	12.9	8.5	2.1	0.00	37.6	170	18	10	
	Jan24_2	6.30	234	29	0.002	4.6	1.1	1.22	5.4	2.2	1.2	5.7	0.010	0.005	2.9	3.6	0.03	17.6	8.4	2.2	0.01	39.3				10
	Jan24_3	6.38	259	35	0.001	4.8	1.1	1.01	5.3	2.3	1.3	5.6	0.010	0.005	2.6	3.9	0.05	19.7	8.5	2.2	0.02	37.8				10
	Jan24_4	6.36	235	40	0.001	4.8	1.5	0.89	5.4	2.4	1.3	5.6	0.011	0.005	2.4	4.1	0.06	22.6	8.4	2.2	0.01	41.4				10
	Jan24_5	6.63	276	43	0.001	5.0	-1.308	0.88	5.4	2.4	1.3	5.6	0.011	0.006	2.3	4.2	0.07	22.0	8.4	2.2	0.01	40.4				7
	Jan24_6	6.61	277	42	0.001	4.9	1.1	0.95	5.4	2.5	1.3	5.5	0.011	0.005	2.3	4.3	0.07	21.3	8.4	2.2	0.01	36.5				2
69	Jan31_1	6.10	265	17	0.002	4.4	0.9	1.37	5.4	2.1	1.2	6.9	0.011	0.005	3.2	3.7	0.02	12.9	8.5	2.1	0.14	37.7	500	6	14	
	Jan31_2	6.15	235	19	0.002	4.6	0.9	1.39	5.3	2.1	1.2	3.9	0.011	0.005	3.1	2.2	0.03	15.0	8.5	2.1	0.15	37.4				14
	Jan31_3	6.54	219	26	0.002	4.4	0.9	1.42	5.3	2.1	1.2	4.0	0.011	0.005	2.9	2.2	0.04	16.5	8.5	3.4	0.41	37.1				14
	Jan31_4	6.67	209	32	0.001	4.5	1.0	1.34	5.3	2.1	1.2	4.4	0.010	0.005	2.6	2.2	0.05	17.9	8.5	2.1	0.16	38.8				8
	Jan31_5	6.78	159	35	0.001	4.5	1.0	1.16	5.3	1.9	1.2	5.1	0.010	0.006	2.1	2.3	0.06	19.3	8.5	2.1	0.20	37.2				3
	Jan31_6	6.46	150	36	0.001	4.5	1.1	1.00	5.3	1.9	1.2	5.4	0.010	0.005	1.9	2.4	0.07	20.0	8.5	2.1	0.15	36.6				3
111	March14_1	6.04	300	16	0.000	4.4	1.0	1.65	5.6	1.8	1.5	8.8	0.010	0.005	4.5	4.3	-0.04	15.0	8.5	2.1	0.15	36.6	700	23	8	
	March14_2	6.26	283	34	0.001	4.6	1.2	1.13	5.7	2.0	1.5	5.8	0.006	-0.003	2.9	4.8	0.00	86.5	8.5	2.1	0.15	35.8				6
	March14_3	6.53	210	48	0.000	4.5	1.4	0.59	5.6	2.0	1.6	9.3	0.006	-0.003	2.3	7.9	0.02	96.2	8.5	2.1	0.18	34.5				3
	March14_4	6.72	138	92	0.000	5.1	1.9	0.36	5.8	2.5	2.2	18.8	0.010	0.000	2.4	18.6	0.06	97.4	8.4	2.1	0.15	27.9				2
	March14_5	6.62	130	86	0.001	4.8	1.9	0.48	5.8	2.5	2.2	15.9	0.010	-0.002	2.4	19.2	0.06	98.2	8.4	2.1	0.17	27.4				2
	March14_6	6.58	136	106	0.001	5.8	2.4	0.66	6.3	2.9	2.9	19.1	0.014	0.000	3.0	35.0	0.10	99.1	8.4	0.7	0.33	15.2				1
119	March22_1	6.03	273	15	0.002	4.2	1.0	1.74	5.8	1.9	1.6	8.6	0.007	-0.002	4.6	4.1	-0.04	100.9	8.5	2.1	0.15	36.7	500	18	15	
	March22_2	6.10	216	29	0.002	4.5	1.0	1.69	5.8	1.9	1.6	8.3	0.008	-0.002	4.4	4.0	-0.03	101.8	8.5	2.1	0.14	36.8				12
	March22_3	6.22	173	25	0.002	4.5	1.0	1.64	5.8	1.9	1.6	8.2	0.008	-0.002	4.3	4.2	-0.03	102.4	8.5	2.1	0.16	36.7				11
	March22_4	6.52	204	26	0.002	4.3	1.0	1.64	5.9	1.9	1.6	8.7	0.008	-0.001	4.0	4.4	-0.02	107.6	8.5	2.2	0.20	36.5				11
	March22_5	6.31	160	30	0.001	4.1	1.0	1.60	5.8	1.9	1.6	8.8	0.008	-0.001	3.5	4.4	-0.02	109.0	8.5	2.2	0.15	36.0				11
	March22_6	6.14	154	30	0.001	4.6	1.0	1.56	5.8	1.9	1.6	8.6	0.007	-0.003	3.3	4.4	-0.02	116.4	8.5	2.1	0.14	35.7				1
132	April4_1	6.20	150	17	0.002	4.5	1.0	1.76	5.8	1.9	1.5	8.4	0.007	-0.001	4.7	4.1	-0.04	60.4	8.4	2.2	0.04	36.1	450	18	8	
	April4_2	6.27	128	18	0.002	4.5	1.0	1.63	5.7	1.8	1.5	6.6	0.007	-0.002	4.2	3.2	-0.03	61.8	8.5	2.2	0.04	36.7				4
	April4_3	6.47	88	26	0.001	4.5	1.0	1.60	5.8	1.8	1.6	8.1	0.008	-0.003	3.6	3.7	-0.03	62.5	8.4	2.2	0.02	36.5				1
	April4_4	6.54	80	30	0.001	4.6	1.0	1.51	5.8	1.9	1.6	9.2	0.007	-0.002	2.8	4.2	-0.02	66.9	8.4	2.3	0.03	34.7				0
	April4_5	6.48	65	33	0.001	4.6	1.1	1.42	5.9	1.9	1.6	9.2	0.006	-0.003	1.7	4.4	-0.02	67.2	8.2	2.2		33.1				0
	April4_6	6.36	51	37	0.001	4.5	1.1	1.29	5.7	1.9	1.6	8.7	0.006	-0.002	0.9	4.4	-0.01	68.9	8.3	2.2	0.02	32.0				0
147	April19_1	6.15	123	16	0.002	4.4	1.0	1.74	5.8	1.9	1.6	8.9	0.007	0.000	4.7	4.3	-0.04	56.3	8.3	2.2	0.03	35.7	200	21	14	
	April19_2	6.32	81	24	0.001	4.5	1.0	1.59	5.8	1.9	1.5	7.9	0.007	-0.002	4.1	4.1	-0.03	56.5	8.2	2.2	0.02	34.9				14
	April19_3	6.53	65	32	0.001	5.4	1.1	1.08	5.7	1.8	1.6	8.8	0.006	-0.002	2.2	4.7	-0.02	56.9	8.1	2.2	0.05	32.4				13
	April19_4	6.60	47	38	0.001	4.5	1.1	1.02	5.8	1.9	1.6	9.2	0.005	-0.001	0.6	4.6	-0.01	58.3	8.0	2.2	0.03	28.2				12
	April19_5	6.67	47	41	0.001	4.5	1.1	0.88	5.7	1.8	1.5	8.8	0.004	-0.001	0.2	4.4	-0.01	58.6	7.9	2.2	0.02	26.6				11
	April19_6	6.60	-32	42	0.001	4.5	1.1	0.82	5.7	1.8	1.6	8.9	0.001	-0.001	0.1	4.1	-0.01	59.5	7.9	2.2	0.11	25.4				2
170	May17_1	6.06	183	19	0.002	4.6	1.1	1.94	5.9	1.8	1.7	8.6	0.009	-0.001	4.9	4.2	-0.04	117.7	8.2	2.2	0.03	35.2	600	24	13	
	May17_2	6.57	154	58	0.001	13.0	1.3	0.68	5.6	2.2	1.6	16.8	0.006	-0.001	1.9	15.2	0.00	117.9	8.2	2.3	0.10	32.5				11
	May17_3	7.06	51	121	0.000	4.6	1.8	0.17	5.4	2.6	2.1	32.0	0.007	-0.001	0.7	38.1	0.03	120.2	10.4	2.2	0.04	26.0				10
	May17_4	6.90	-43	153	0.001	5.2	2.4	0.37	5.6	3.2	2.8	30.7	0.011	0.003	0.4	54.9	0.06	121.3	11.2	2.3	0.04	18.9				7

day	Sample ID	pH	Eh	alkalinity HCO3 mg/l	Be mg/l	Na mg/l	Mg mg/l	Al mg/l	Si mg/l	K mg/l	Mn mg/l	Fe mg/l	Co mg/l	Ni mg/l	Zn mg/l	As mg/l	Sr mg/l	Ca mg/l	F mg/l	Cl mg/l	NO3 mg/l	SO4 mg/l	flow ml/min	temperature celcius	pressure psi	
	May17_5	6.70	-57	167	0.001	5.4	2.6	0.69	5.8	3.7	3.1	23.0	0.011	0.004	0.2	61.1	0.06	121.5	10.6	2.5	0.02	17.8				4
	May17_6	6.59	-22	179	0.001	5.8	2.7	0.88	6.0	4.0	3.2	22.4	0.010	0.005	0.1	69.9	0.08	121.7	7.7	2.6	0.02	10.8				1
184	May31_1	6.18	200	30								9.7			4.1	4.2			8.9	1.8	0.05	37.5	300	25		8
	May31_2	6.27	164	32								10.2			3.7	4.4			8.7	1.7	0.12	37.3				8
	May31_3	6.34	151	35								10.6			3.1	4.6			8.7	1.7	0.06	36.8				7
	May31_4	6.45	141	37								10.8			2.1	4.7			8.7	1.8	0.09	35.9				7
	May31_5	6.47	135	43								10.4			0.9	4.7			8.6	1.8	0.05	34.5				4
	May31_6	6.52	128	44								10.3				4.8			8.7	1.8	0.07	33.5				2
198	June14_1	6.00	113	20	0.004	5.2	1.0	1.82	5.5	3.1	1.6	7.2	0.268	0.268	4.6	3.6	0.12	15.4	8.9	1.7	0.05	37.3	100	30	10	
	June14_2	6.44	20	55	0.004	6.3	1.1	1.09	5.4	3.0	1.6	17.5	0.268	0.268	2.4	10.1	0.12	22.0	8.8	1.8	0.17	34.6				6
	June14_3	6.78	-50	85	0.004	8.9	1.4	1.07	5.3	3.3	1.9	25.2	0.268	0.268	1.4	23.0	0.12	29.6	9.8	1.7	0.08	29.3				4
	June14_4	6.73	-31	145	0.004	11.2	1.6	1.07	5.3	3.5	2.1	22.9	0.268	0.268	1.0	31.8	0.12	34.1	10.3	1.7	0.09	23.5				3
	June14_5	6.61	-13	102	0.004	13.0	1.8	1.07	5.4	3.5	2.3	17.4	0.268	0.268	0.5	36.5	0.12	36.8	10.0	1.7	0.09	15.0				3
	June14_6	6.53	6	88	0.004	12.6	1.8	1.16	5.4	3.5	2.2	14.2	0.268	0.268	0.2	35.9	0.12	37.1	8.3	1.7	0.10	10.8				1
218	July4_1	6.15	188	19	0.004	5.1	1.0	1.80	5.4	3.2	1.6	11.8	0.268	0.268	4.3	5.1	0.12	14.9	8.8	3.0	2.07	37.2	450	26	13	
	July4_2	6.29	156	22	0.004	7.7	1.3	1.84	5.7	3.2	1.6	10.8	0.268	0.268	4.0	4.9	0.12	18.2	8.6	1.9	0.66	37.4				11
	July4_3	6.38	141	39	0.004	8.6	1.4	1.66	5.5	3.2	1.6	9.6	0.268	0.268	3.5	4.7	0.12	20.4	8.7	1.9	0.39	37.3				11
	July4_4	6.42	135	37	0.004	12.2	1.7	1.87	5.8	3.3	1.6	9.8	0.268	0.268	3.2	4.8	0.15	22.2	8.9	1.9	0.09	37.4				8
	July4_5	6.49	148	45	0.006	94.1	14.1	19.85	20.2	4.5	2.1	46.5	0.268	0.268	18.6	5.4	0.31	39.4	8.6	2.1	0.18	36.8				5
	July4_6	6.54	145	16	0.004	14.0	1.9	1.48	5.6	3.3	1.6	8.3	0.268	0.268	2.2	4.8	0.23	25.7	8.5	1.8	0.09	36.8				0
233	July19_1	6.89	97	23	0.004	5.4	1.1	1.76	5.4	3.0	1.7	11.2	0.268	0.268	4.3	4.3	0.12	14.7	8.6	2.3	0.03	35.4	610	22	12	
	July19_2	6.78	43	29	0.004	6.0	1.1	1.70	5.5	3.3	1.6	10.6	0.268	0.268	4.0	4.4	0.12	17.3	8.6	2.3	0.08	36.1				11
	July19_3	5.94	-207	35	0.004	7.4	1.3	1.69	5.5	3.1	1.6	10.6	0.268	0.268	3.7	4.6	0.12	19.1	8.6	2.3	0.06	36.0				11
	July19_4	6.01	-175	36	0.004	-1.0	0.4	1.07	1.8	2.7	0.5	3.4	0.268	0.268	1.1	1.3	0.12	7.1	8.6	2.5	1.2	36.4				10
	July19_5	6.16	-200	38	0.004	8.8	1.4	1.63	5.6	3.1	1.6	10.0	0.268	0.268	2.9	4.4	0.12	21.0	8.7	2.3	0.12	36.1				7
	July19_6	6.23	-253	34	0.004	8.7	1.4	1.56	5.5	3.1	1.5	9.8	0.268	0.268	2.6	4.3	0.12	21.4	8.7	2.2	0.04	36.0				2
258	Aug13_1	6.19	234	20	0.00	4.7	1.1	1.17	5.8	2.8	1.7	8.7	0.05	0.04	4.7	4.3	0.02	16.8	8.6	2.2	0.05	35.5	340	22	8	
	Aug13_2	6.48	180	45	0.00	4.1	1.3	1.10	5.8	2.8	1.6	8.5	0.05	0.04	2.6	4.6	0.10	21.4	8.6	2.2	0.04	36.8				5
	Aug13_3	6.61	160	44	0.00	4.7	1.8	0.87	5.9	2.9	1.5	8.8	0.05	0.04	1.7	6.0	0.18	23.2	8.5	2.3	0.07	35.4				5
	Aug13_4	6.59	134	50	0.00	4.7	2.1	0.60	5.8	2.7	1.4	8.2	0.05	0.04	1.0	6.5	0.23	27.9	8.4	2.2	0.07	34.7				2
	Aug13_5	6.72	111	57	0.00	4.8	2.6	0.33	5.8	2.8	1.4	8.0	0.05	0.04	0.8	7.4	0.28	30.9	8.2	2.2	0.04	34.0				2
	Aug13_6	6.77	110	64	0.00	4.2	2.7	0.30	5.8	2.9	1.4	7.6	0.05	0.04	0.6	8.2	0.30	32.2	8.4	2.7	0.12	33.6				0
261	Aug16_1	6.20	266	18	0.00	4.8	1.3	1.39	5.7	2.8	1.7	8.6	0.05	0.04	4.3	5.4	0.05	19.3	8.5	2.3	4.58	35.4	100	23	12	
	Aug16_2	7.22	259	41	0.00	4.7	1.4	1.36	5.7	2.6	1.5	8.6	0.05	0.04	1.7	4.6	0.13	24.6	8.3	2.3	0.08	35.2				9
	Aug16_3	7.86	256	58	0.00	4.7	2.0	0.32	5.7	2.9	1.6	9.4	0.05	0.04	0.8	7.5	0.22	30.5	8.3	2.3	0.06	33.9				7
	Aug16_4	8.13	256	111	0.00	5.2	3.3	0.29	5.4	3.1	2.0	10.4	0.05	0.04	0.6	16.6	0.35	41.3	8.8	2.3	0.06	25.4				4
	Aug16_5	8.06	255	116	0.00	5.1	3.4	0.32	5.5	3.1	1.9	8.3	0.05	0.04	0.3	15.6	0.39	41.6	8.6	2.3	0.05	19.6				2
	Aug16_6	8.00	256	116	0.00	5.0	3.2	0.38	5.6	3.0	1.7	7.9	0.05	0.04	0.6	11.8	0.34	38.4	8.3	2.3	0.07	14.1				0
268	Aug23_1	6.04	189	24	0.00	4.6	1.1	1.38	5.8	2.7	1.7	12.2	0.05	0.04	4.7	5.5	0.02	16.6	8.6	2.2	0.05	36.4	380	18	12	
	Aug23_2	6.16	172	35	0.00	4.8	1.1	1.12	5.8	2.9	1.7	12.1	0.05	0.04	4.4	5.5	0.03	18.9	8.8	2.2	0.05	36.4				11
	Aug23_3	6.20	142	35	0.00	4.5	1.2	1.32	5.8	2.7	1.7	12.1	0.05	0.04	4.2	5.5	0.03	20.1	8.7	2.2	0.05	36.4				11
	Aug23_4	6.25	141	36	0.00	4.7	1.2	1.17	5.8	2.7	1.7	12.2	0.05	0.04	3.9	5.5	0.04	21.2	8.7	2.2	0.05	36.2				11
	Aug23_5	6.28	133	40	0.00	4.7	1.3	1.08	5.8	2.7	1.7	11.9	0.05	0.04	3.6	5.5	0.05	22.1	8.8	2.2	0.08	36.0				8
	Aug23_6	6.30	134	41	0.00	4.7	1.3	1.36	5.8	2.7	1.7	11.8	0.05	0.04	3.4	5.5	0.05	22.4	8.7	2.2	0.08	36.0				2
274	Aug29_1	6.20	160	25	0.00	4.3	1.1	1.58	5.7	2.7	1.7	12.4	0.05	0.04	4.6	5.5	0.02	16.4	8.7	2.2	0.08	35.9	430	32	13	
	Aug29_2	6.34	138	30	0.00	4.3	1.1	1.02	5.7	2.7	1.7	12.1	0.86	0.04	4.3	5.5	0.02	18.3	8.7	2.2	0.15	35.9				13
	Aug29_3	6.38	131	36	0.00	4.4	1.2	1.47	5.8	2.8	1.7	12.2	0.05	0.04	4.1	5.6	0.03	19.8	8.7	2.2	0.09	36.3				13
	Aug29_4	6.40	118	37	0.00	4.1	1.2	1.24	5.7	2.8	1.7	11.9	0.05	0.04	3.7	5.6	0.03	20.5	8.7	2.2	0.16	36.2				10
	Aug29_5	6.44	122	40	0.00	4.4	1.3	1.08	5.7	2.8	1.7	11.7	0.06	0.04	3.4	5.7	0.04	21.6	8.7	2.2	0.16	37.1				0
	Aug29_6	6.46	122	43	0.00	4.4	1.3	1.25	5.7	2.8	1.7	11.7	0.05	0.04	3.2	5.7	0.04	22.8	8.6	2.2	0.08	35.6				2
280	Sept4_1	6.19	176	25	0.00	4.3	1.1	1.24	5.7	2.7	1.7	11.6	0.05	0.04	4.6	5.2	0.02	16.3	8.7	2.4	0.06	35.8	520	20	7	
	Sept4_2	6.27	168	30	0.00	4.3	1.1	1.42	5.7	2.7	1.7	12.2	0.06	0.04	4.5	5.5	0.02	18.1	9.1	2.4	0.12	37.1				6
	Sept4_3	6.32	157	33	0.00	4.3	1.2	1.27	5.8	2.7	1.7	12.2	0.05	0.04	4.3	5.6	0.02	18.9	8.7	2.4	0.08	35.9				6
	Sept4_4	6.38	145	33	0.00	4.3	1.2	1.21	5.7	2.7	1.7	12.2	0.05	0.04	4.2	5.5	0.03	19.7	8.7	2.4	0.09	35.8				6
	Sept4_5	6.41	142	36	0.00	4.4	1.2	1.17	5.7	2.8	1.7	12.0	0.05	0.04	4.0	5.5	0.03	20.4	8.8	2.4	0.06	35.8				3
	Sept4_6	6.45	139	38	0.00	4.4	1.2	1.19	5.7	2.7	1.7	12.1	0.05	0.04	3.9	5.6	0.03	21.0	8.7	2.5	0.13	35.6				1
287	Sept11_1	6.14	267	24	0.00	4.3	1.1	1.10	5.8	2.7	1.7	12.3	0.05	0.04	4.6	5.6	0.02	16.5	8.8	2.4	0.06	36.1	520	20	13	
	Sept11_2	6.16	241	30	0.00	4.3	1.1	1.24	5.7	2.7	1.7	12.3	0.05	0.04	4.5	5.5	0.02	17.6	9.2	2.5	0.11	37.3				12
	Sept11_3	6.22	224	33	0.00	4.3	1.2	1.24	5.7	2.7	1.7	12.1	0.05	0.04	4.4	5.5	0.02	18.5	8.8	2.3	0.07	35.9				12
	Sept11_4	6.29	203	36	0.00	4.3	1.2	1.22	5.7	2.7	1.7	12.3	0.05	0.04	4.2	5.5	0.03	19.3	8.8	2.4	0.08	35.9				10
	Sept11_5	6.32	199	37	0.00	4.3	1.2	1.14	5.8	2.7	1.7	12.2	0.05	0.04	4.0	5.5	0.03	20.3	8.8	2.4	0.11	35.8				4
	Sept11_6	6.36	199	40	0.00	4.3	1.2	1.02	5.7	2.7	1.7	12.1	0.05	0.04	4.0	5.5	0.03	20.8	8.8	2.4	0.09	35.7				1
294	Sept18_1	5.72	254	23	0.00	4.7	1.1	0.63	6.1	2.7	1.8	9.3	0.05	0.04	4.6	4.6	0.02	16.7	8.8	2.6	0.16	36.2	480	18	7	
	Sept18_2	5.87	231	23	0.00	4.7	1.1	0.76	6.0	2.8	1.8	9.3	0.05	0.05	4.5	4.3	0.02	18.3	9.1	2.5	1.99	37.2				7
	Sept18_3	5.96	223	23	0.00	4.7	1.2	0.81	6.0	2.7	1.8	9.6	0.05	0.04	4.4	4.4	0.02	19.7	8.9	2.4	0.1	36.1				7
	Sept18_4	5.96	216	37	0.00	4.7	1.3	0.80	5.9	2.7	1.8	9.7	0.05	0.04	4.3	4.4	0.03	20.9	8.8	2.7	0.15	36.0				6
	Sept18_5	6.05	205	37	0.00	4.8	1.3	0.68	5.8	2.7	1.8	9.5	0.05	0.04	4.2	4.4	0.03	21.9	8.8	2.4	0.09	36.0				4
	Sept18_6	6.22	195	37	0.00	4.8	1.3	0.82	5.8	2.8	1.8	9.8	0.05	0.04	4.1	4.4	0.03	23.0	8.8	2.4	0.08	35.9				1
301	Sept25_1	5.83	254	20	0.00	4.7	1.1	0.77	5.8	2.7	1.7	10.6	0.05	0.04	4.8	4.7	0.02	16.7	8.9	2.5	0.07	35.5	440	20	11	
	Sept25_2	5.82	241	17	0.00	4.7	1.1	0.84	5.8	2.8	1.7	10.6	0.05	0.04	4.6	4.7	0.02	18.0	9.2	2.5	0.12	37.1				9
	Sept25_3	5.94	234	31	0.00	4.7	1.2	0.77	5.8	2.8	1.7	10.8	0.05	0.04	4.5	4.8	0.02	19.1	8.7	2.5	0.15	36.2				8
	Sept25_4	5.97	226	34	0.00	4.6	1.2	0.81	5.8	2.8	1.7	10.9	0.05	0.04	4.3	4.8	0.03	20.2	9.0	2.4	0.11	35.1				4
	Sept25_5	6.12	216	43	0.00	4.8	1.3	0.83	5.8	2.8	1.8	10.9	0.05	0.04	4.2	4.9	0.03	21.6	8.7	2.4	0.12	36.0				1
	Sept25_6	6.07	212	37	0.00	4.7	1.3	0.65	5.7	2.8	1.7	11.2	0.05	0.04	4.1	4.9	0.03	22.3	8.7	2.4	0.08	35.8				

Concentrations for Cu, Cr, Cd, Pb, and Sb are not included in the Appendix because they were consistently below the detection limit of the lowest standard used

Concentrations for PO4 are not included in the Appendix because they were also below the detection limit for the lowest standard